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THE ORGAN OF THE

Society of Public Analysts and other Analytical Chemists

A MONTHLY JOURNAL DEVOTED TO THE ADVANCEMENT
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Errata

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P. 127. The figure referred to in line 13 is Fig. 2 (not Fig. 1) in the original paper.

P. 136. The figure referred to in line 25 is Fig. 2 (not Fig. 1) in the original paper.

P. 154, line 3. *For* "200 mgrms." *read* "300 mgrms."

Pp. 244–247. In the tables the expression "Mean 1·25SD Mean 2SD" *should read* "Mean *minus* 1·25SD Mean *minus* 2SD."

P. 717, line 4 from the bottom. *For* "Trtilek" *read* "Irtilek."

P. 854, line 7 from the bottom. *For* "years" *read* "yards."

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THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

An Ordinary Meeting of the Society was held at the Chemical Society's Rooms, Burlington House, on Wednesday, December 6th, the President, Mr. F. W. F. Arnaud, in the chair.

Certificates were read in favour of Sydney Emsley, B.Sc., F.I.C., George Frederick Hall, M.B.E., B.Sc., A.I.C., Walter Maurice Keightley, A.I.C., Dorothy Mary Mathews, B.Sc., Reginald Percival Page, F.I.C., Hilda Mary Perry, M.Sc., A.I.C., Arthur Dudley Powell, A.I.C., Winifred Ethel Smith, B.Sc., A.I.C.

The following were elected members of the Society:—Willard E. Baier, B.S., Adam Dunsmore, A.I.C., Donald Clarence Garratt, B.Sc., Ph.D., F.I.C., Colston James Regan, B.Sc., F.I.C., Robert Henry Slater, D.Sc., Ph.D., F.R.S.E., A.I.C.

The following papers were read and discussed:—"A Specific Gravity Apparatus," by the late C. H. Cribb, B.Sc., F.I.C. (read by T. McLachlan, F.I.C.); "The Excretion of Aloes," by G. F. Hall, M.B.E., B.Sc., A.I.C., and W. M. Keightley, A.I.C.; "The Chemical Examination of Furs in Relation to Dermatitis. Part IV. The Chemical Reactions of Dyeing with *p*-Phenylenediamine and *p*-Aminophenol," by H. E. Cox, M.Sc., Ph.D., F.I.C.; "The Use of the Air-Damped Balance for the Determination of Total Solids in Milk," by John Golding, D.S.O., F.I.C.; "A Rapid Method of Determining Minute Quantities of Nitrites," by G. G. Rao and K. M. Pandalai.

NORTH OF ENGLAND SECTION

A meeting of the Section was held in Sheffield on December 2nd, 1933. The Chairman (Mr. John Evans) presided over an attendance of thirty. Dr. J. T. Dunn gave an account of the appearance, before the Departmental Committee on Food Law, of the Society's representatives.

The following papers were read and discussed:—"Note on Nitrates in Milk," by W. F. Elvidge, B.Sc., F.I.C.; "The Effect of Certain Salts in Fermentation in Dough," by R. M. Callow, M.Sc., A.I.C.; and "Note on Freezing-point Determinations," by E. V. Jones, F.I.C.

Death

WITH deep regret we record the death, on December 11th, of William Partridge. An obituary notice will be published later.

Obituary

ALFRED EDWARD JOHNSON

ALFRED EDWARD JOHNSON, who died on the 30th September, at the age of 75, was educated at the City of London School, and subsequently, from 1878 to 1881, he was at the Royal College of Science, Ireland, where he obtained his Associateship.

In 1883 he went to Wolverhampton as assistant to the late E. W. T. Jones, and continued to hold that post until Mr. Jones's death in 1922. He then went into partnership with the writer, with whom he was appointed Joint Public Analyst for the County of Stafford and the Boroughs of Stoke-on-Trent, Wolverhampton, and Newcastle-under-Lyme, which appointments they held until October, 1929. At that date, upon the County Council setting up their own laboratory, the partnership was dissolved, Mr. Johnson taking over the whole work of the above-mentioned boroughs.

He obtained his F.I.C. in 1888, and in 1901 gained the London B.Sc. degree. In 1923 he joined the Society of Public Analysts, and was elected a member of the Council for 1931–32.

Mr. Johnson made a valuable contribution to chemical literature in the excellent *Analyst's Laboratory Companion*, of which he was the author, and which is now in its fifth edition. In collaboration with Mr. W. Lincoln Sutton he revised the tenth and eleventh editions of *Volumetric Analysis* by Francis Sutton, and also contributed several articles to the *Chemical News*.

He was an able analyst, always willing to give help to another, and was a most industrious and conscientious worker, who carried on his work to the day of his death.

Mr. Johnson was exceedingly musical, being an accomplished organist and pianist. He leaves a widow and one son.

ERNEST V. JONES

The Chemical Examination of Furs in Relation to Dermatitis

BY H. E. COX, M.Sc., PH.D., F.I.C.

PART IV

THE CHEMICAL REACTIONS OF DYEING WITH *p*-PHENYLENEDIAMINE AND *p*-AMINOPHENOL

(*Read at the Meeting, December* 6, 1933)

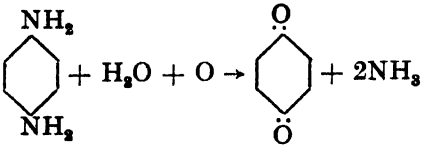
IN previous papers of this series it has been shown, as a result of investigating a large number of cases of fur dermatitis, that at least 45 per cent. of these cases were due to *p*-phenylenediamine-dyed furs. There are good reasons for knowing that this particular fur base is concerned in a still higher percentage, and is more important than all the other potential causes put together. For this reason a detailed study of this substance, its properties and those of its oxidation products has been made, with the object of gaining some slight knowledge of the mysterious phenomenon of idiosyncrasy, and of determining whether the dye itself acts as the primary irritant or only through certain intermediate oxidation products. Is the action of *p*-phenylenediamine a normal chemical action? Is a fur dyed with it potentially irritant because of any free diamine or because of the chance presence of some special bye-product which is peculiarly irritant? Moreover, the properties of this, the most important member of the fur-dye group, are likely to differ only in detail from those of the other amino compounds which are used.

Some account has already been given (ANALYST, 1933, **58**, 743) of *p*-phenylenediamine in relation to its transfusion through living and dead tissue, and of its reactions with blood or serum and substances occurring therein. It is the purpose of the present paper to discuss the identity of the dye formed on fur treated with *p*-phenylenediamine or *p*-aminophenol, and also to determine what bye-products are actually formed, and so may be present in an imperfectly dyed or washed fur; the properties of these bye-products are considered in so far as they bear on the causation of dermatitis.

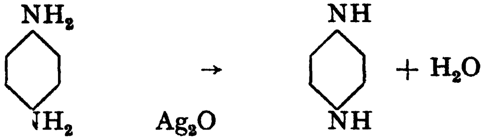
Little has been published on the chemistry of fur dyeing; it has generally been assumed that the black dye is Bandrowski's base, though Austin (*Fur Dressing and Dyeing*, p. 163) does suggest an azine type without giving any reference to experimental evidence for it, and A. G. Perkin, in an appendix to Dr. Parsons's report on the subject in 1924, states that the further stages of colour development are unknown, but the final product is probably a complex azine, as in the case of aniline black.

In considering the possible products of oxidation of diamines on furs, certain conditions must be borne in mind which limit the range of possible reactions. These are that: (1) the temperature must always be low, not exceeding approximately blood heat; (2) the liquors must not be acid or strongly alkaline; and

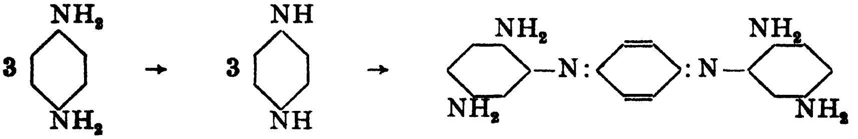
(3) the oxidising agent in practice is nearly always hydrogen peroxide, though dichromate, copperas, copper sulphate and other metallic compounds may be used as mordants. Traces of bleaching powder may occasionally be included. In strongly acid solution the oxidation of *p*-phenylenediamine yields quinone and ammonia almost but not quite quantitatively (*cf.* Erdmann, *Ber.*, 1904, **37**, 2908; Green and Johnson, *ibid.*, 1913, **46**, 3772) thus:



If neutral solutions are employed and water is rigorously excluded, the product of mild oxidation is quinone di-imine, which substance is at once decomposed by water (*cf.* Willstätter and Pfannenstiel, *Ber.*, 1904, **37**, 4605)



In weakly alkaline solutions, with hydrogen peroxide, there are several products of which the best known is tetra-aminodiphenyl-*p*-azo-phenylene, well known as Bandrowski's base.



Erdmann (*loc. cit.*) indicates that about 80 per cent. of this black base is formed, but Heiduschka and Goldstein (*Arch. Pharm.*, 1916, **254**, 584), who studied it in detail, show that, at best, only about 30 per cent. of the black base results; even in the presence of excess of peroxide some 50 per cent. of the diamine remained unchanged, and there was a residuum of about 20 per cent. of non-identified products. All these published experiments deal with the pure diamine, and do not take into consideration the complicating effects of the presence of animal fibre. In my experiments, examples of which follow, some idea of the nature of the dye has been obtained, and a quantitative determination of the oxidation products has been made, so that all the products are known, and approximately 100 per cent. of the diamine used is accounted for.

The Composition of the Dye on the Fur.—It has been shown (by Heiduschka) that the maximum yield of black dye is obtained when about three molecular proportions of hydrogen peroxide are used to one of *p*-phenylenediamine. I find when this is done that there always remains a slight excess of peroxide in the liquid, so that more would be useless. This corresponds with the general directions for using fur dyes, which include about 15 parts of 10 volume peroxide to 1 part of the intermediate; this ratio leads to a fairly pure form of Bandrowski's base, whether fur be present or not. For the quantitative study of the reaction I have taken advantage of the fact that Bandrowski's base is almost insoluble in water, but freely soluble in hot pyridine, so that it can be filtered out of the liquor extracted from the fur, and its purity controlled by observation of the m.pt. This procedure gives a clear filtrate, in which the total nitrogen can be determined and the forms in which it is present ascertained by the ordinary methods of analysis; they were proved to be unoxidised *p*-phenylenediamine, with traces of quinone and ammonia. There remains the fur. It is found to be strongly dyed, and the dye is not extractable by any solvent—including pyridine, 60 per cent. acetic and formic acids—and can only be removed by decomposing the hair with caustic soda. Subsequent acidification enables one to examine it in the usual way to ascertain, not its entire constitution, but at least its class and general reactions. It is found that the pigment in a fur dyed in the usual way consists of three parts:

(i) Bandrowski's base *on* the fibre; (ii) an insoluble azine combined *in* the fibre with the protein substance; (iii) a small quantity of azine *on* the fibre.

The products remaining in the dye bath consist of: (iv) Bandrowski's base in suspension; (v) Bandrowski's base in solution; (vi) free *p*-phenylenediamine; (vii) a small amount of ammonia; (viii) a small amount of quinone; (ix) a small excess of hydrogen peroxide.

The following details of an experimental dyeing, which follows the general instructions given with fur dyes, show the quantitative relationships. Sodium carbonate was used in place of ammonia (which is more usual) because of the complicating effect of ammonia in the subsequent analyses.

Ten grms. of rabbit fur, clipped from the hide so as to eliminate difficulties due to skin and its protein or fats, were soaked for 24 hours in a bath containing copper sulphate 2 grms., acetic acid 1 grm., water 500 ml. Next day the fur was removed and rinsed.

Determination of the copper showed that the fibre had absorbed 0·4 per cent. of its weight of copper (as Cu)—an observation which gives an indication of the amount of mordant likely to be found in black dyed fur.

The fur was then immersed in a dye-bath made from *p*-phenylenediamine, 4·00 grms.; sodium carbonate (dry), 1·50 grm.; water, 400 ml.; and 60 ml. of hydrogen peroxide (10 vol.) were added. After 24 hours at 25° C. the fur was collected on muslin, well squeezed out and washed in repeated changes of water, until substantially free from *p*-phenylenediamine. The total volume of liquor amounted to 1100 ml. This was filtered; the insoluble base, which weighed 0·935 grm., was found to have m.pt. 237° C., and to give all the reactions of Bandrowski's base; it consisted of fairly pure base. The total nitrogen, determined on the filtrate, was found to be equivalent to 1·27 grm. of *p*-phenylenediamine. Hence it follows that the fur contained altogether the equivalent of 1·77 grm. of the diamine in water-insoluble forms. The liquid was examined qualitatively, and found to contain traces of peroxide, ammonia, quinone and much unoxidised *p*-phenylenediamine. Determination of the quantity of the *p*-phenylenediamine by Callan and Henderson's method failed, owing to the interference of the other substances, but it was readily determined by weighing the quinone dichloro-di-imine formed with sodium hypochlorite, and was found to amount to 0·590 grm. Ammonia was determined by distillation with magnesia as usual, and found to be

0·10 grm., which with its equivalent quinone is equal to 0·36 grm. of *p*-phenylenediamine. Quinone was determined by titration of the iodine liberated from potassium iodide in acid solution; its quantity was 0·40 grm.

It was also needful to examine the dyed fur; this weighed 11·6 grms.; it was extracted with hot pyridine in a Soxhlet extractor until the extracts were almost colourless; this yielded 0·690 grm. of a black powder which melted at 235° C., showing it to be Bandrowski's base, but there was a small residuum of black compound which had m.pt. not below 280° C. The extracted fur now contained 1·06 grm. of a black dye which was not soluble in any solvent. The colour of the fibre was as black after the extraction of the Bandrowski's base as before; evidently the real dye is not this base (see below). The base extracted with pyridine was boiled with *N* hydrochloric acid which, as has been shown, decomposes and dissolves Bandrowski's base, and the insoluble compound was filtered off (weight, 0·042 grm.); it had m.pt. not below 280° C., and the reactions described below indicated that it was an azine. These results may be expressed as a balance sheet and show that the *p*-phenylenediamine added is completely accounted for within experimental error.

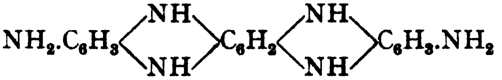
p-Phenylenediamine			Per cent. of diamine added
Added	Found		
4·00 grms.	as unoxidised diamine	0·59	14·8
	as Bandrowski base in suspension	0·95	23·8
	as ammonia and quinone	0·36	9·0
	as Bandrowski base in solution	0·18	4·5
	as azine *in* the fur	1·08	27·0
	as Bandrowski base *on* the fur	0·67	16·8
3·87	as azine *on* the fur	0·04	1·0
Unaccounted for 0·13 grm.	Total	3·87	96·9

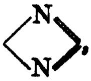
Other experiments of a like kind have been made, and the results definitely indicate that the final product is an azine combined with the protein of the fur. A large excess of peroxide does not improve the result, but yields more insoluble azine outside the fibre.

One or two practical points may be mentioned. In neither Bandrowski's base nor the azine can the nitrogen be accurately determined by the Kjeldahl method. I have tried several modifications, including the well-known Jodlbauer procedure, but the results are always low. (Heiduschka also mentions that the direct Kjeldahl process is inapplicable to this base, but apparently did not try modifications.) Bandrowski's base, when dissolved in pyridine, gives a deep red solution which forms an intense blue with hydrochloric acid. The azine is practically insoluble, and forms no colour on the addition of acid. It is decolorised by hydrosulphite or titanous chloride, but re-oxidises readily in air.

PROPERTIES OF THE DYED FUR.—Fur which is coloured only with Bandrowski's base externally can be readily recognised either by extracting the base with hot pyridine or by decomposing the base on the fibre by boiling with dilute hydrochloric acid. This method is applicable to most furs on which stripes have been dyed by the familiar paint-brush procedure. But when the azine stage is reached it is found that nothing is yielded, even to boiling pyridine or on treatment with acid or with any other solvent. The azine character of the dye is only determinable by decomposing the fibre with caustic soda, then acidifying and reducing with titanous chloride or boiling the fibre with the usual sodium formaldehyde sulphoxylate solution. It is then decolorised, but the colour is at once restored on exposure to air, as is characteristic of azines.

Experiments on the quantitative reduction to the leuco base have been made by boiling some of the fur containing a known weight of the azine with caustic soda, then acidifying with hydrochloric acid, adding pyridine and titrating with titanous chloride in an atmosphere of carbon dioxide. It was found that the amount of hydrogen required to reduce it was only 0·18 per cent. by weight. This observation seems to disprove the formula suggested by Austin:



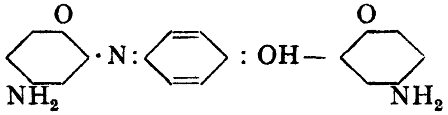
since the addition of even one hydrogen atom would require 0·31 per cent. of the element. In order that 0·2 per cent. of hydrogen may suffice to form the leuco compound, the substance must have a molecular weight of at least 500. As it has been shown that there are no side-products, except in quite small traces, it follows that the structure of the azine must be a multiple of the three molecules of Bandrowski's base; this implies nine benzene rings as a minimum. It has been shown by Green and others that the aniline blacks have chains of as many as eleven benzene rings. The oxidation product of *p*-phenylenediamine must have at least nine, and, of course, the azine structure requires the grouping , in which at least one nitrogen is free, and can take up a hydrogen atom to form a leuco compound. This does not appear in Austin's suggested formula.

Experiments have also been made to ascertain whether dyeing could be effected by means of Bandrowski's base, whether this substance is the necessary intermediate product in the production of the azine, and whether it can be further oxidised without the presence of fur or other organic matter. If this base is the intermediate product and no side reactions occur, it forms additional evidence of the number of rings in the structure of the azine; it must be a multiple of three. A quantity of finely-powdered Bandrowski's base was suspended in water, and kept warmed at blood-heat with excess of hydrogen peroxide; there was found an azine not melting below 300° C. and resembling that already described, and no other products were detected by analytical processes. Evidently the azine is capable of being formed direct from the base without side-reactions. Heiduschka and his colleague observed that when they oxidised *p*-phenylenediamine with excessive quantities of peroxide at high temperatures they obtained mixtures which they could not analyse; evidently these included the azine and Bandrowski's base, as well as the products already enumerated. This experiment also suggests the presence of multiples of three benzene rings in the structure of the azine.

It was not found possible to dye fur by soaking it in a suspension of the Bandrowski's base with excess of peroxide; it is clearly necessary for the *p*-phenylenediamine or the base to be absorbed into the hair substance and oxidised therein.

A successful dyeing experiment was effected by dissolving 1 grm. of the base in 20 ml. of pyridine, then soaking fur (2 grms.) in it, adding 20 ml. of water, and later 10 ml. of hydrogen peroxide; under these conditions Bandrowski's base enters the protein substance, and is oxidised therein, with the production of the azine. The colour of fur so dyed is similar to, but weaker than, that dyed directly with *p*-phenylenediamine, so that this method affords a method of dyeing without the direct application of *p*-phenylenediamine, and would appear entirely to preclude the possibility of the presence of the free amine. There are certain obvious reasons why such a method presents difficulties in commercial practice; if they could be overcome, cases of fur dermatitis would arise less frequently.

DYEING WITH *p*-AMINO-PHENOL.—In order to ascertain whether the azine formation just described is a general result of the oxidation of fur dyes, another set of experiments was made, using *p*-amino-phenol instead of *p*-phenylenediamine. When oxidised in acid solution, this substance is converted quantitatively into quinone, and in solution in dry ether it is convertible into quinone mono-imine by silver oxide, but, when oxidised in alkaline solution by air or hydrogen peroxide, it forms a compound of which the detailed structure does not appear to have been elucidated. Bandrowski, who first described it (*Monatsh.*, 1889, **10**, 124), gives $C_{18}H_{15}(NO)_3$. It is a dark brownish-black crystalline substance which melts at 228° C., and there are reasons for thinking it may have the formula:



A fur dyed with *p*-amino-phenol will usually contain some of this base, but the true pigment is found to be an oxazine analogous with the azine produced from *p*-phenylenediamine. A quantitative study of the distribution of the amino-phenol has been made following the same procedure as has been already described, except that the unoxidised amino-phenol was determined by Powell's method (ANALYST, 1919, **44**, 52) as quinone chloro-imine, which is formed on adding hypochlorite to the acid solution and is more soluble than the dichloro-di-imine. The clipped fur, mordanted with copper, was treated with *p*-amino-phenol in exactly the same manner as in the *p*-phenylenediamine experiments. The results were as follows:

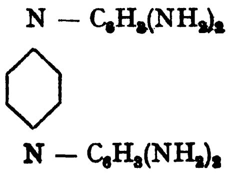
	p-Amino-phenol		
Added	Found		Amine added Per Cent.
4·00 grms.	as unoxidised amine	1·91	47·7
	as base in suspension	0·54	13·5
	as ammonia and quinone	0·42	10·5
	as base in solution	0·18	4·5
	as oxazine in the fur	0·53	13·2
	as base on the fur as oxazine on the fur	0·64	16·0
4·22			
Error +0·22		4·22	105·4

The pyridine-extracted fur dyed with the oxazine is of a deep brown colour—not black; the dye is not extractable by solvents and undergoes the same changes with reagents as the azine dye formed from *p*-phenylenediamine. Analogy indicates that the pigment is an oxazine resembling the azine formed from the diamine.

The significance of these observations in relation to fur dyeing and dermatitis lies in the demonstration that the true object of the fur-dyeing process is the formation of this azine in the fur fibre itself, and not merely the development of Bandrowski's base, as has hitherto been supposed by writers on this subject. The ideal process should form the azine and subsequently remove not only any remaining unoxidised amino compound, but also the base which is loose on the fibres. Clearly, if this be done, there can be no question of any dermatitis developing from irritant properties of the fur. I have examined several hundred dyed furs in detail and find that this objective is attained only in quite a small percentage of cases. A fur in which Bandrowski's base is present, but no free diamines, may be truly said to be well dyed and washed, but it is a less perfect product than one in which all the dye is fast. Patterns, such as lines or spots, are often dyed on to fur by a sort of painting process, in which the peroxide is applied also with a brush; it is manifestly very difficult, if not impossible, to secure complete azine formation in such circumstances.

In Part II of this series (ANALYST, 1933, **58**, 738) it was mentioned that in 12, out of about 216 furs, it had not been possible to identify the actual fur base used. When the amount of the dye is small and the colour not very dark, it appears that the whole of the original intermediate may have been converted into the azine or oxazine and so become completely insoluble. This state of affairs is readily recognisable, but, as the dye compound cannot be split up or re-formed into its original components by ordinary means, it becomes impossible to recognise the original amine. This probably accounts for the cases not identified.

DECOMPOSITION OF BANDROWSKI'S BASE.—In earlier parts of these papers reference has been made to the re-formation of free *p*-phenylenediamine from Bandrowski's base by action of hydrochloric acid, and figures were given showing the approximate extent of such reaction (Cox, *J. Soc. Dyers and Color.*, 1932, **48**, 124), which was referred to as hydrolysis. It is difficult to see just how a compound of the formula



can be re-formed into $C_6H_4(NH_2)_2$ without the presence of a reducing agent to supply hydrogen. When wool or fur is present this may happen readily enough. The reaction has now been investigated further, and it is found that, on boiling Bandrowski's base with dilute (*N*) hydrochloric acid, *p*-phenylenediamine hydrochloride is the principal product, and there are also formed ammonia, hydroquinone, hydrogen cyanide and carbon dioxide.

It has been shown that this liberation of *p*-phenylenediamine does not occur as a result of exposure either to water or to perspiration, but the reaction is of practical importance from the analyst's point of view, because it shows that a fur must not be extracted with warm mineral acid, or there may be produced a whole range of substances which were not already there—including *p*-phenylenediamine, quinone, hydroquinone and cyanide; hence an erroneous conclusion as to the method of dyeing might be reached.

The action of hydrochloric acid in this way is also of theoretical interest, as it involves the unusual phenomenon of a breaking down, not only of a quinone group, but actually of a benzene ring, by so simple a reagent as dilute hydrochloric acid. It is being further investigated, and I hope to discuss it in detail on another occasion. It may be remarked, however, that Heiduschka and Goldstein (*loc. cit.*) found that, although a definite salt was formed with sulphuric acid, they were unable to say what happened when hydrochloric acid was used. They noted the bright red colour which develops at an early stage, but did not isolate any compounds.

OTHER OXIDATION PRODUCTS.—It remains to consider what oxidation products other than Bandrowski's base and the azine may be produced, and whether any of them are liable to be present in imperfectly treated fur. Various substances are suggested from time to time, notably quinone di-imine. I propose to comment only on a few substances, considering whether they are specially irritant, and what evidence that they are ever present in dyed fur.

It has been shown that quinone is a minor bye-product of the oxidation, and, of course, hydroquinone is easily formed from it. Quinone is very irritating to the nose and throat, and in alkaline solution is an active reducing agent*; it seems likely that it might cause skin irritation if present, but as a result of the examination of very many furs dyed with *p*-phenylenediamine, which have been definitely known to have caused dermatitis, I have never found any quinone or quinol, and I do not think these are ever likely to be present unless as actual ingredients of a dyeing mixture; it is easily washed out or removed in the finishing processes.

Quinone di-imine is known to be the immediate precursor of Bandrowski's base; it is very poisonous when taken internally (*cf.* Erdmann, *Ber.*, 1904, **37**, 2908). I prepared this substance by the method of Willstätter and Pfannenstiel (*loc. cit.*), and have described some of its reactions with blood in Part III. It is almost instantly decomposed by water, forming the usual insoluble black base with no free *p*-phenylenediamine. It thus appears impossible that it should ever be present in a dyed fur; it would not be detected by the ordinary processes of analysis, but could be extracted with anhydrous ether, in which it forms a yellowish solution which gives a brown-black solid on the addition of a few drops of water. To test its effect on the skin, I applied an ethereal solution of the di-imine first on the back of a mouse. The mouse suffered no apparent inconvenience; the imine quickly formed a brownish black stain by absorption of moisture from the air, but, on later killing the animal and preparing sections of the skin, no evidence was obtainable of any penetration even of the ethereal solution; the outer layer of the epidermis was stained, but there was no penetration or apparent effect on the cells underneath. Having satisfied myself by experiments on mice, I applied a few drops of a concentrated ethereal solution of the di-imine to my own arm; a brown stain was quickly formed, which subsequently became almost black, but there was no irritation at all.

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* Quinone is commonly regarded as an oxidising agent, but in alkaline solution it quickly reduces Fehling's solution, silver nitrate or permanganate solution.

Quinone dichloro-di-imine ($C_6H_4N_2Cl_2$) has been under suspicion in the minds of one or two writers. That it should be present pre-supposes the use of bleaching powder or sodium hypochlorite as the oxidising agent. So far as I know, these are never used in ordinary practice. The substance is readily prepared by adding sodium hypochlorite to a slightly alkaline solution of *p*-phenylenediamine; it is nearly insoluble in water; suspended in water and acidified with nitric acid it does not give any precipitate with silver nitrate; on boiling with dilute nitric acid quinone is formed, which is easily recognisable by its odour or colour reactions, and a chloride reaction is obtainable. In this way it can be easily detected, if present on a fur. Applied to the skin, it had no apparent effect.

I have searched for this substance in many furs, but have never found any to be present. It is my opinion that *p*-phenylenediamine itself, and not any intermediate oxidation products, is the active irritant in fur dermatitis.

SUMMARY OF PART IV.—A quantitative study of the oxidation of *p*-phenylenediamine with hydrogen peroxide in the presence of fur shows that the principal pigment formed is an azine combined with the fur proteins. Some Bandrowski's base is found on the surface of the fibres, and there exists in the solution in the dye bath much free unoxidised *p*-phenylenediamine, together with some Bandrowski's base and traces of quinone and ammonia. Similar data are given in respect of *p*-amino-phenol, which forms an oxazine in an analogous manner. The azine from *p*-phenylenediamine forms a leuco compound, with the addition of only 0·18 per cent. of hydrogen, by action of titanous chloride; it can be formed by direct oxidation of Bandrowski's base in solution, and has at least nine benzene rings in its constitution.

A preliminary account is given of the reaction of Bandrowski's base with dilute hydrochloric acid, whereby free *p*-phenylenediamine is formed. This base is not, as has usually been assumed, the desired product in fur dyeing. The occurrence and properties of the other intermediate oxidation products are discussed in relation to dermatitis.

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Acidimetry of Wines

By JAMES HOSSACK

In the analysis of wine the usual practice is to make determinations of the "total acids" and of the "volatile acids" independently, while the "fixed acids" are calculated by difference. This practice does not commend itself to the writer. The usual defence for it seems to be summarised in a short passage in Allen's "Commercial Organic Analysis" (5th Ed., Vol. 1, p. 228), where the contention is made that a determination of "fixed acids" is of necessity inaccurate. The reasons given appear illogical. A little clear thinking will show that the term "fixed acids" can be more rigidly defined than can the term "volatile acids." The latter are separated by steam distillation. The point at which this operation should be suspended is often one of convention only. The exact result may be affected by the rate at which the steam is driven, and by other factors. Acid remaining after evaporating on the water-bath and drying at 105° C. is a much more definite quantity.

The real cause of discrepancy in the past seems to have been as much the uncertainty of end-points in titration as anything else. When red wines in particular are to be titrated for "total acids," an external indicator is generally used. European practice seems to favour litmus paper. In the U.S.A. azolitmin solution (essentially "refined litmus") should be employed, though in certain cases a mixture of solid phenolphthalein with sodium sulphate may be substituted. (*Vide* "Methods of Analysis," A.O.A.C., 3rd Ed., p. 140.)

Neither litmus nor any of its constituents is a reliable indicator when organic acids are being titrated, and any end-point obtained externally is likely to lack precision.

When the determination of "fixed acids" is made on such materials as are here under discussion, there is the same end-point difficulty as for "total acids." When "volatile acids" are being determined, the point at which steam distillation is to cease may also be uncertain.

If the trouble due to colouring matter could be overcome and a suitable internal indicator used, good independent determinations of all three factors could be made. If only two were considered necessary the "total" and "fixed" acids could be determined more quickly and conveniently than "volatile" acids. With these ideas in mind the writer has worked out the following procedure:

TOTAL ACIDS.—Measure 50 ml. of the wine to be tested into a 250 ml. graduated flask, add 10 ml. of saturated barium chloride solution, then 50 ml. of $N/10$ sodium hydroxide solution free from carbonates and sulphates. Almost all natural colouring matter will be precipitated. Make up to the mark with water (free from carbon dioxide), mix well and filter through a rapid paper. Reject the first 10 ml. of filtrate, and from the remainder pipette 100 ml. into a separate flask for titration. Acidify by adding 25 ml. of $N/10$ hydrochloric acid, then titrate back with $N/10$ sodium hydroxide solution in the usual manner, using phenolphthalein solution as indicator. The end-point is quite distinct.

An approximately $N/10$ solution of sodium hydroxide which will automatically maintain its freedom from carbonates is most conveniently obtained by adding to 100 ml. of normal sodium hydroxide approximately 10 ml. of saturated barium chloride solution, diluting to 1 litre and decanting the clear liquid (or, if necessary, filtering through a rapid paper) before standardisation. Such a solution is best not used in titration against sulphuric acid, though the presence of sulphates in the wine will not cause error.

FIXED ACIDS.—Evaporate 50 ml. of wine to dryness on the water-bath. Finish drying in an oven at 105° C. Dissolve the residue in a convenient amount of water, transfer to a graduated 250-ml. flask and proceed as for the determination of "Total Acids" described above.

CALCULATION OF RESULTS.—If X = ml. of $N/10$ NaOH used in the final titration, then 20 ml. of wine contain (X − 5) ml. of $N/10$ acid. This can be converted further to such terms as the analyst may prefer.

For purposes of comparison, analyses of four wines are given below. All determinations were made directly, "total" and "fixed" acids as above, "volatile" as described in "Methods of Analysis, A.O.A.C., 3rd Ed., p. 140, "Method I." Samples 1 and 2 were fortified sweet red wines (port type), No. 3 was an unclarified fortified yellow wine (sherry type), and No. 4 was a spoiled wine (red Burgundy type). Results are expressed as ml. of $N/10$ acid equivalent to 20 ml. of wine.

Sample No.	Total acid found	Fixed acid found	Volatile acid found
1	19·9	16·5	3·36
2	20·3	16·0	4·28
3	18·4	12·7	5·80
4	19·0	14·8	4·08

The figures in the last column are 2/5 of those read from the burette on titration, since a conventional 50-ml. sample was taken for distillation.

When this method of analysis is applied to fruit juices, or to wines, the total acidity of which is greater than decinormal, larger volumes of alkali than those here mentioned must be added before the filtration. Precipitation of the colouring matter can only be assured in alkaline solution.

If thymol blue is substituted for phenolphthalein in these determinations, a direct titration of the aliquot portion of the filtrate against $N/10$ hydrochloric acid may be made with advantage, somewhat simplifying both the procedure and the calculation, but the latter indicator is so much more popular that it was thought best to adapt the directions to its peculiarities.

If barium hydroxide is substituted for sodium hydroxide, no barium chloride need be used at any point. The merits of barium hydroxide in many routine operations do not seem to be appreciated at the present day.

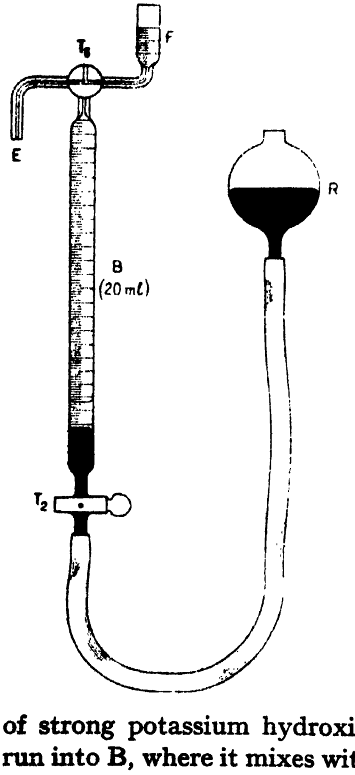
The thanks of the writer are due to Dr. Alfred Tingle, Chief of the Customs-Excise Laboratory, for making possible the performance of the work here recorded and for suggestions which have contributed to a successful issue.

CUSTOMS-EXCISE LABORATORY
DEPARTMENT OF NATIONAL REVENUE
OTTAWA, CANADA

A Rapid Colorimetric Method for the Detection and Determination of Small Quantities of Oxygen in Gases

By H. R. AMBLER, Ph.D., F.I.C.

A colorimetric method has been worked out for the detection of oxygen in mixed gases, and for its determination where present in quantities between 0·01 and 0·5 per cent. The volume of sample required is 20 ml. or less, depending on the oxygen-content.



The principle of the process depends on the colour imparted by oxygen to alkaline pyrogallol solution, which is compared with that of iodine solution of known strength (Pfeiffer, *J. für Gasbeleuchtung*, 1897, **40**, 354).

The apparatus used is shown in the diagram. B is a burette of about 20 ml. capacity, fitted at the bottom with a tap, T_2, and at the top with a three-way tap, T_1, which can be set to connect any two (or all three) of the following:—the burette, B, a funnel, F, of about 2 ml. capacity, and the gas entrance, E. It is desirable, but not essential, for B, and also F, to be graduated in tenths of a ml.; the tap and the connections should be about 1·5 mm. in bore. T_2 is connected by pressure-tubing with a mercury-reservoir, R.

At the beginning of an analysis, B and the bore of T_1 contain mercury only. A small volume of a freshly prepared aqueous solution of pyrogallol (1 : 3) is placed in F, and a measured amount (say, 0·3 ml.) is run into the burette through T_1; F is now washed out with dilute acid and water successively, these being expelled through E; a small quantity of strong potassium hydroxide solution is placed in F, and about 0·6 ml. of this run into B, where it mixes with the pyrogallol. It is advisable at this stage to wash out F with dilute acid and water as before.

The solutions in B are further mixed by inverting the burette with T_1 and T_2 closed. The mixed solution should be almost colourless; with good distilled water and reagents this result can be attained without any special precautions.

E is now connected with the source of the gas to be tested; if an ample supply of this is available it is blown off through F until the connections have been cleared of all air; T_1 is then turned so as to connect E with B, and the appropriate volume of gas is drawn into B. If the amount of gas sample is limited it is best contained in a vessel such as the Huntly sampler (Huntly, *J. Soc. Chem. Ind.*, **1910, 29, 312**), fitted with a three-way tap, the common end of which is close-connected with E by rubber tubing, and the connections are cleared of air by running mercury from F through the three-way tap of the sampler.

When the required volume of gas (20 ml. or less) has been taken, T_1 is turned so as to close B, T_2 is closed, and the burette is inverted once or twice to ensure complete absorption of the oxygen. The colour of the solution is then matched with iodine; this is most conveniently done by running *N*/10 iodine solution, drop by drop, from a burette into a small measuring cylinder of the same diameter as B, previously containing a small volume of water (say, 1 ml.). The iodine solution contains two parts of potassium iodide to one of iodine (Pfeiffer, *loc. cit.*). The colour matching should be done in fairly strong transmitted light, and at a standard time, say two minutes after admission of the gas.

From the strength of the solution of iodine matching the pyrogallol solution the amount of oxygen is derived by an empirical relation, which, for precise work, should be determined under the exact conditions of normal use with gases of known oxygen content, For approximate work, the relation given in the following table may be used:

Volume of oxygen (at N.T.P.) absorbed by unit volume of mixed solution	Iodine solution of equal colour depth
0·01	0·01 *N*.
0·02	0·025
0·03	0·04
0·04	0·055
0·05	0·065
0·06	0·08
0·07	0·095

Within the range of the above figures good colour matches are obtainable. For strengths above about 0·1 *N* iodine the solutions are too deep in colour for accurate matching, whilst below 0·01 *N* the colours are appreciably different in quality. For a considerable way below this strength, however, the colour of the pyrogallol solution is sufficient to provide a definite qualitative test. The range may be extended in both directions by varying the volumes of reagent and of gas sample. Ferric chloride, and also mixtures of ferric, copper and cobalt salts have been tried as comparison solutions, but are found to have no advantage over iodine.

The principle of the method was applied originally to coal-gas (Pfeiffer, *loc. cit.*), hydrogen, hydrocarbons and oxides of carbon not interfering. Nitrous oxide, also, has been found not to interfere. Hydrogen sulphide (which gives a red colour) and oxidising gases, such as chlorine, must not be present.

RESEARCH DEPARTMENT
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The Analysis of Magnesium Alloys

By L. C. NICKOLLS, M.Sc., D.I.C., A.R.C.S., A.I.C.

THE analysis of magnesium alloys presents no difficulties except when the alloys contain aluminium. As most common commercial alloys do contain aluminium it has been necessary to devise methods for determining aluminium in the presence of comparatively large quantities of magnesium. Blum (*Sci. Papers*, No. 286, *Bureau of Standards*) has shown that precipitation of the aluminium hydroxide is dependent on the p_H value of the solution lying within narrow limits, while Lassieur (*Compt. rend.*, 1926, **182**, 384) has stated that, provided that the p_H value of the solution does not exceed 7·0, aluminium may be separated completely from magnesium by precipitation with ammonia as hydroxide. There is more difficulty in separating these metals when the ratio of the magnesium to the aluminium is as high as is usually found in commercial magnesium alloys, and Hackney (*Quantitative Analysis of Inorganic Materials*, p. 322) states that such a separation is practically impossible. Berg (*Z. anal. Chem.*, 1927, **71**, 369) and others have used 8-hydroxyquinoline to effect a separation, but the use of this reagent usually hinders the direct determination of other metals possibly present.

A method has been employed in the Government Laboratory which is free from this defect and is superior to the precipitation at a known p_H value of the aluminium as hydroxide with ammonia. It depends upon the fact that alkali sulphides precipitate aluminium hydroxide from solutions of aluminium salts, whilst magnesium gives the soluble hydrosulphide. There is no tendency to co-precipitation, although the p_H value of the solution is about 7·5. The only difficulty is the mechanical one of washing the bulky aluminium hydroxide precipitate free from magnesium salts. Excess of ammonium chloride does not appear to be necessary to keep the magnesium in solution, which agrees with the results of Lassieur (*loc. cit.*), but we have considered it advisable not to dispense with it.

PROCEDURE IN THE ABSENCE OF MORE THAN TRACES OF MANGANESE, ZINC OR NICKEL.—In the absence of manganese, nickel or zinc in considerable amount, a comparatively simple method is adopted. One grm. of the alloy is dissolved in 1:1 hydrochloric acid containing a little nitric acid or bromine, and the solution is evaporated on the water-bath to dryness to fix the silica. The chlorides are taken up in 100 ml. of hot water, sufficient hydrochloric acid to dissolve the magnesium oxychloride and 20 grms. of ammonium chloride are added, and the silica is filtered off, ignited, and weighed. Hydrogen sulphide is passed through the filtrate, and the precipitated Group II sulphides are filtered off and examined in the usual manner. Usually there is only a trace of copper. To the filtrate, which should smell of hydrogen sulphide, ammonia is added until the liquid turns a dark green colour, due to ferrous sulphide, and a precipitate is formed. Hydrochloric acid is then carefully added, with stirring, until the precipitate just dissolves, but the dark tint of the iron sulphide is not entirely discharged. Five ml. of 6 *N* sodium sulphide solution are added, hydrogen sulphide is passed to saturate the solution, and the beaker is heated on the water-bath for an hour. The precipitate is filtered off and well washed with dilute ammonium nitrate solution to remove magnesium salts. Calcium, strontium and barium may be determined in the filtrate by precipitation with ammonium carbonate. The filter paper and precipitate are returned to the beaker, 20 ml. of hydrochloric acid and a few ml. of bromine water are added, and the beaker is heated on the water-bath to dissolve the precipitate. This solution now contains all the iron, aluminium and the traces of manganese, nickel and zinc. The iron, aluminium and manganese are precipitated by adding ammonia, heating the liquid to boiling, filtering, and igniting the precipitate in the blowpipe flame. The iron is determined by fusing the precipitate with potassium bisulphate, extracting with water, and titrating with titanous sulphate solution, and its amount is deducted from the weight of alumina. Nickel is determined in the filtrate with dimethyl glyoxime, and the zinc in the filtrate from the nickel is determined with pyridine thiocyanate. When manganese is present it should be determined on a separate portion with sodium bismuthate and the necessary amount deducted from the weight of the ignited alumina. The magnesium in the sample is obtained by difference.

MODIFIED PROCEDURE IN THE PRESENCE OF MANGANESE, ZINC OR NICKEL.—In the presence of comparatively large amounts of zinc, manganese or nickel, the adjustment of the neutrality of the solution after filtering off Group II sulphides is more difficult. Zinc and manganese sulphides do not dissolve until the solution is distinctly acid. Instead of adding hydrochloric acid, as previously, till the precipitate just disappears, it is best, after the liquid has been made slightly ammoniacal, to add hydrochloric acid until the tint of the iron sulphide begins to fade, then to add the sodium sulphide solution, and to continue as before. Nickel gives an intensely black insoluble precipitate which completely obscures the neutral point. When nickel is present, ammonia is slowly added until a permanent black precipitate is formed, and then 2 or 3 more drops are added before the treatment with sodium sulphide. The filtrate from the alumina in all these cases should be tested by adding a little ammonia to ensure that the iron has been completely precipitated. It is advisable, moreover, when zinc, manganese or nickel is present in considerable quantity, or if more than 7 per cent. of aluminium is present, to dissolve the precipitate and repeat the sodium sulphide separation. The double precipitation does not require much more time, since it is not necessary to wash the first precipitate free from chlorides. The mixed precipitate is treated as described above for the determination of the various metals present.

EXPERIMENTAL.—The method was tested by adding known amounts of alum solution to a solution of four grms. of magnesium chloride in water together with, in certain cases, some zinc, nickel or manganese salts. The results for aluminium tended to be slightly high, even though the precipitated alumina was ignited in a muffle furnace. When tested for magnesium, however, by fusing the alumina with potassium bisulphate, dissolving the mass in dilute sulphuric acid, and precipitating the magnesium as phosphate in ammoniacal tartrate solution, it was shown that magnesium was absent. It should be pointed out that Hahn and Scheiderer (*Ber.*, **1924**, **57**, **1854**) state that magnesium in small amount is not precipitated under these conditions. Our experiments have shown, however, that one per cent. of magnesium in aluminium can be accurately determined as phosphate in ammoniacal tartrate solution, and that 0·5 per cent. can be determined with substantially accurate results, provided that the solution is allowed to stand for 48 hours. The absence of a positive test for magnesium on the alumina precipitate shows, therefore, that the percentage of magnesium is less than the experimental error.

The results are given only to the first decimal place, as it is not considered that the second place has any significance.

	Percentage of aluminium	
	Added	Found
One precipitation	10·0	10·5, 10·3, 10·4, 10·2, 10·6
	8·0	8·5, 8·3, 8·3, 8·4
	6·5	6·6, 6·7, 6·7, 6·5, 6·5
	5·0	5·0, 5·0, 5·0, 4·9
Two precipitations	9·9	9·9, 9·9, 10·0
	7·9	8·0, 8·0, 8·1
Nickel present (one precipitation)	5·0	5·4
„ „ (two precipitations)	5·0	5·0
Zinc „ (one precipitation)	5·0	5·1
Manganese „ („ „)	5·0	4·9

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Nitron as a Precipitant for Nitrates

BY J. E. HECK, H. HUNT, AND M. G. MELLON

(Contribution from the Department of Chemistry, Purdue University)

THE entrainment* of material by precipitates formed in solution presents one of the most disturbing problems confronting the analytical chemist, particularly when he is concerned with gravimetric precipitation processes. That the matter has had serious attention is evident from the literature, where one may find much work relating to the analytical significance of the phenomenon.

In recent years there has been an increasing use of various organic compounds as precipitating agents, such as benzidine, cupferron, dinitroresorcinol, 8-hydroxyquinoline, nitron, nitroso-β-naphthol, phenylthiohydantoic acid, pyridine and salicylaldoxime. In view of the voluminous character and the complex structure of some of the precipitates formed by certain elements with these precipitants, it seemed that the specific surfaces and polarities of the compounds formed might be such as to exhibit interesting entraining capacities.

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* Entrainment is used in the general sense, without any commitment regarding the specific nature of the mechanism of the process involved.

Saylor[1] concluded that, in some degree, all solid substances entrain from their mother liquor ions of electrolytes, molecules of solvent and dissolved non-electrolytes. The extent of this entrainment is known to vary greatly for different substances and for different conditions,[2] but we are without sufficient basis for calculating it quantitatively in any given cases. France[3] stated that no simple rule has yet been found that enables one to predict what foreign materials will be appreciably entrained by any given crystalline substance.

The object of this study was to determine whether precipitates, such as those mentioned above, entrain certain cations, and, if so, whether the magnitude of contamination is sufficient to influence seriously the precision of analytical determinations. In addition, an inspection of part of the previous work indicated, for some of the precipitates at least, the desirability of checking the reproducibility of individual determinations and the reliability of the methods under different conditions.

From the organic reagents available, nitron, a precipitant for the nitrate radical, was chosen for the first work. This compound seemed particularly promising, on account of the possibility of oxidising and volatilising the precipitate of nitron nitrate, leaving as a residue only material which had been entrained or incompletely removed during washing. This residue could then be examined spectroscopically or taken up in a solvent and tested colorimetrically. Nitron nitrate is appreciably soluble, and must, therefore, be treated with only a limited amount of washing medium. For this reason it was thought foreign material might be present from incomplete washing, if not from entrainment.

On account of the solubility of nitron nitrate Gutbier[4] expected low results with the method. Not finding this to be the case, he concluded that nitron acetate, the precipitant, might have been "occluded" sufficiently to compensate for the solubility. The results of others[5], from the time when the method was originally proposed by Busch, have indicated disagreement concerning errors, both in magnitude and direction. Some agreed well with what theoretically should have been obtained, even when the precipitation occurred in the presence of various other constituents, as reported by Vasiliev; some were low and some were appreciably high, as reported by Hes.

EXPERIMENTAL WORK

MATERIAL AND APPARATUS.—The salts were recrystallised, except ferric chloride, which was prepared by passing dry chlorine gas over heated pieces of pure iron wire.[6] Conductivity water was used to prepare the solutions. To determine their metallic content, portions of 25 or 50 ml. were analysed by standard methods, as given in the reference for each of the following elements: Aluminium,[7] barium,[8] cadmium,[9] cobalt,[10] copper,[11] iron,[12] lead,[13] magnesium,[14] nickel,[15] potassium,[16] and sodium.[17] From the content of metal found the equivalent content of nitrate was calculated. The analytical data are not included.

A freshly prepared and filtered 10 per cent. solution of nitron in 5 per cent. acetic acid served as the precipitant.

The spectroscopic examination of precipitates was made by means of a Hilger instrument (E-3), with the use of an arc-spectrum and ortho plates.* To identify the metals, a search was made for their "persistent" lines in spectrograms according to the procedure of Holt.[18]

PRECIPITATIONS.—For precipitating the nitron nitrate Gutbier's modification[4] of Busch's original procedure[5] was used in most of the work. A solution containing about 0·12 grm. of nitrate in 100 ml., acidified with 12 to 15 drops of dilute sulphuric acid (2 : 3), was heated almost to boiling. To this were added, all at one time, 12 ml. of a 10 per cent. solution of nitron in 5 per cent. acetic acid. After being cooled to room temperature the beaker was placed in ice-water for an hour and a half. The precipitate was quickly transferred to a porcelain crucible with porous bottom, small portions of the filtrate being used to remove the last traces of precipitate. For the washing, not more than 12 ml. of ice-cold water were used, 2 to 3 ml. at a time, and the precipitate was drained as completely as possible after each washing. Finally, the precipitate was dried at 105° C., and the nitrate was calculated by means of the theoretical factor 0·1653. In some cases acetic or hydrochloric acid was substituted for sulphuric acid, the latter being unsuitable for the nitrates of lead or of the alkaline earths because of the low solubility of the corresponding sulphates.

Since both Gutbier[4] and Treadwell and Hall[19] suggested a possible "occlusion" of precipitant by the precipitate, the process of precipitation was reversed in certain cases to determine the effect upon the weight of precipitate found. No other direct means of testing this source of entrainment suggested itself.

By adding to the solution of a nitrate a salt having the same cation, but a different anion, a few precipitations were made in the presence of a concentration of cation greater than that equivalent to the nitrate present. A few precipitations were also made in solutions containing mixtures of several salts likely to be encountered in ordinary analyses, as others have found that from a mixture of electrolytes a particular ion is entrained less than if present alone. Furthermore, entrainment of a cation is influenced by the nature of the anion present.

Two modifications of the procedure were tried, one due to Vasiliev[5] and the other to Treadwell and Hall.[19] In the former the precipitate was washed mainly with a cold, saturated solution of nitron nitrate, and finally with 3 to 5 ml. of ice-cold water. In the latter the precipitate stood for 24 hours in the dark at room temperature before filtration, after which it was filtered off and washed with 50 ml. of a saturated solution of nitron nitrate at room temperature. In this case an empirical factor 0·1679 was used.

As a check on the gravimetric method with nitron nitrate several determinations were made by means of two adaptations of the Kjeldahl method and by Kolthoff's new method.[20, 21, 22] For all these titrimetric procedures 25 ml. of a solution of sodium or potassium nitrate were used.

Of the various methods tried for decomposing the nitron nitrate, preparatory to testing for entrained cations, the most workable procedure was heating with a mixture of concentrated sulphuric and nitric acids.[23] Since it proved long and troublesome, however, it was discarded in most of the work in favour of direct spectrographic examination. Examinations were made of precipitates obtained from each solution of a pure nitrate and from all solutions in which changes of acidity or other constituents were made, 0·01 grm. samples being used.

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* The spectroscopic examination was made by H. Hunt.

In order to obtain more concentrated samples the organic matter was completely oxidised, by the method mentioned above, in 0·3 grm. samples of a few precipitates obtained from solutions containing mixtures of salts. The inorganic residue was dissolved in a small amount of dilute hydrochloric acid and transferred to the anode.

A summary of the results for all precipitations made of nitron nitrate and of evidence of entrainment of cations found on examination of the respective precipitates is given in Table I. Table II contains the comparative results for the several methods of determining the nitrate radical.

TABLE I

DATA FOR PRECIPITATES OF NITRON NITRATE

No. of detns.	Cation added Grms.	Weight of NO_3		Maximum deviation from mean Grm.	Difference Grm.	Acid used			Spectroscopic evidence
		Assumed present Grm.	Average found Grm.			Kind	Vol.	Conc.	
Aluminium nitrate									
4		0·1186	0·1177	±0·0003	−0·0009	H_2SO_4	15 dps.	2:3	No Al
Barium nitrate									
1		0·1193	0·1191		−0·0002	HCl	25 ml.	0·2 *N*	
1*		0·1193	0·1190		−0·0003	HCl	25 ml.	0·2 *N*	No Ba
1	0·133 Ba(*a*)	0·1193	0·1193		0·0000	HCl	25 ml.	0·2 *N*	Tr. Ba
1*	0·133 Ba	0·1193	0·1188		−0·0005	HCl	25 ml.	0·2 *N*	
Cadmium nitrate									
2		0·1239	0·1225	±0·0000	−0·0014	H_2SO_4	15 dps.	2:3	Tr. Cd
2	0·110 Cd(*b*)	0·1239	0·1224	±0·0001	−0·0015	H_2SO_4	15 dps.	2:3	Tr. Cd
Cobalt nitrate									
2		0·1182	0·1178	±0·0001	−0·0004	H_2SO_4	15 dps.	2:3	Tr. Co
2*		0·1182	0·1175	±0·0002	−0·0007	H_2SO_4	15 dps.	2:3	Tr. Co
Copper nitrate									
2		0·1460	0·1443	±0·0000	−0·0017	HOAc	10 ml.	0·5 *N*	Tr. Cu
2		0·1460	0·1440	±0·0004	−0·0020	HOAc	50 ml.	0·5 *N*	Tr. Cu
2		0·1477	0·1453	±0·0001	−0·0024	HCl	25 ml.	0·2 *N*	Tr. Cu
2	0·122 Cu(*c*)	0·1477	0·1454	±0·0000	−0·0023	HCl	25 ml.	0·2 *N*	Tr. Cu
Potassium nitrate									
4		0·1202	0·1192	±0·0001	−0·0010	H_2SO_4	15 dps.	2:3	No K
2		0·1202	0·1195	±0·0001	−0·0007	No acid used			No K
2	0·038 K(*d*)	0·1202	0·1194	±0·0001	−0·0008	No acid used			No K
Magnesium nitrate									
2		0·1199	0·1193	±0·0001	−0·0006	H_2SO_4	15 dps.	2:3	No Mg
2		0·1348	0·1337	±0·0002	−0·0011	HCl	25 ml.	0·2 *N*	No Mg
3	0·053 Mg(*e*)	0·1348	0·1338	±0·0003	−0·0010	HCl	25 ml.	0·2 *N*	No Mg
2	0·133 Mg	0·1348	0·1338	±0·0001	−0·0010	HCl	25 ml.	0·2 *N*	No Mg
2		0·1348	0·1333	±0·0000	−0·0015	H_2SO_4	15 dps.	2:3	No Mg
2		0·1348	0·1334	±0·0001	−0·0014	HOAc	10 ml.	0·5 *N*	No Mg
2		0·1348	0·1334	±0·0001	−0·0014	HOAc	50 ml.	0·5 *N*	No Mg
2	0·061 Cu(*c*)	0·1348	0·1339	±0·0001	−0·0009	HCl	25 ml.	0·2 *N*	Tr. Cu

TABLE I—*continued*

No. of detns.	Cation added Grms.	Weight of NO_3		Maximum deviation from mean Grm.	Difference Grm.	Acid used			Spectroscopic evidence
		Assumed present Grm.	Average found Grm.			Kind	Vol.	Conc.	
				Nickel nitrate					
3		0·1197	0·1193	±0·0003	−0·0004	H_2SO_4	15 dps.	2:3	Tr. Ni
1*		0·1197	0·1193		−0·0004	H_2SO_4	15 dps.	2:3	
1	0·057 Ni (*f*)	0·1197	0·1199		+0·0002	H_2SO_4	15 dps.	2:3	
1*	0·057 Ni	0·1197	0·1191		−0·0006	H_2SO_4	15 dps.	2:3	Tr. Ni
				Sodium nitrate					
4		0·1201	0·1194	±0·0001	−0·0007	H_2SO_4	15 dps.	2:3	
2	0·016 Al(*g*) 0·057 Ni(*f*) 0·061 Cu(*h*)	0·1201	0·1197	±0·0001	−0·0004	H_2SO_4	15 dps.	2:3	Tr. Ni Tr. Cu
2	0·016 Al(*g*) 0·057 Ni(*f*) 0·061 Cu(*h*)	0·1201	0·1196	±0·0002	− 0·0005	H_2SO_4	15 dps.	2:3	Tr. Ni Tr. Cu
2	0·133 Mg(*e*) 0·057 Ni(*f*) 0·061 Cu(*h*)	0·1201	0·1197	±0·0001	−0·0004	H_2SO_4	15 dps.	2:3	Tr. Ni Tr. Cu
2	0·133 Mg(*e*) 0·057 Ni(*f*) 0·061 Cu(*h*)	0·1201	0·1192	0·0000	−0·0009	H_2SO_4	15 dps.	2:3	Tr. Ni Tr. Cu
2	0·133 Ba(*a*) 0·485 Pb(*i*)	0·1201	0·1199	±0·0002	−0·0002	HCl	25 ml.	0·2 *N*	No Ba No Pb
2	0·133 Ba(*a*) 0·047 Fe(*j*)	0·1201	0·1191	±0·0003	− 0·0010	HCl	25 ml.	0·2 *N*	Tr. Fe
2	0·047 Fe(*j*)	0·1201	0·1196	±0·0001	−0·0005	H_2SO_4	15 dps.	2:3	Tr. Fe
2	0·047 Fe	0·1201	0·1192	±0·0001	−0·0009	H_2SO_4	15 dps.	2:3	Tr. Fe
				Lead nitrate					
2		0·1192	0·1194	±0·0001	+0·0002	HCl	25 ml.	0·2 *N*	No Pb
2*		0·1192	0·1195	±0·0002	+0·0003	HCl	25 ml.	0·2 *N*	No Pb
2	0·485 Pb(*i*)	0·1192	0·1190	±0·0001	−0·0002	HCl	25 ml.	0·2 *N*	No Pb
2		0·1192	0·1192	±0·0000	0·0000	HOAc	10 ml.	0·5 *N*	No Pb
2	0·970 Pb	0·1192	0·1194	±0·0001	+0·0002	HCl	25 ml.	0·2 *N*	No Pb
2	0·970 Pb	0·1192	0·1190	±0·0003	−0·0002	HOAc	10 ml.	0·5 *N*	No Pb
2		0·1192	0·1192	0·0000	0·0000	HOAc	50 ml.	0·5 *N*	No Pb

* Solution of the nitrate added at boiling temperature to the solution of the nitron.

Cations added in the form of the salts indicated:—(*a*) $BaCl_2$; (*b*) $CdSO_4$; (*c*) $CuSO_4$; (*d*) K_2SO_4; (*e*) $MgSO_4$; (*f*) $NiCl_2$; (*g*) $Al_2(SO_4)_3$; (*h*) $Cu(C_2H_3O_2)_2$; (*i*) $Pb(C_2H_3O_2)_2$; and (*j*) $FeCl_3$.

DISCUSSION OF RESULTS.—The significance of the data presented may be considered from two view-points: (i) Evidence of entrainment by the precipitate of nitron nitrate, and (ii) evidence bearing upon the general reliability of the method for the gravimetric determination of the nitrate radical.

The two sources of entrainment considered here were cations present in the solution from which the precipitate separated, and the precipitant itself, nitron. An inspection of the results presented in Table I and of the spectrogram shows little evidence of the presence, in the precipitate, of appreciable amounts of the metals present at the time of precipitation. The order of mixing solution and precipitant did not affect the results of these tests. Even in the case of the concentrated samples the amounts of metals detected were still quantitatively unimportant. In nearly all cases the spectrograms showed more sodium and silicon than the other constituents which it was thought might be present. For this reason precipitates obtained from sodium nitrate were not examined spectroscopically for sodium.

Table II

The Nitrate in Nitrates by Different Methods

		Nitrate			
No. of detns.	Method	Assumed present Grm.	Average found Grm.	Maximum deviation (±) from mean Grm.	Difference Grm.
4	Gutbier–Busch	0·1201*	0·1191	0·0001	−0·0010
6	Devarda alloy	0·1201*	0·1154	0·0004	−0·0047
5	Moore	0·1201*	0·1142	0·0007	−0·0059
4	Vasiliev–Busch	0·1200†	0·1194	0·0000	−0·0006
4	Treadwell–Hall	0·1200†	0·1201	0·0001	+0·0001(E)
		0·1200†	0·1183	0·0001	−0·0017(T)
4	Kolthoff	0·1200†	0·1193	0·0005	−0·0007

* Determined by calculation from the amount of sodium sulphate obtained from a portion of 25 ml. of the solution of sodium nitrate.

† Weighed directly as potassium nitrate.

(E) Using the empirical factor 0·1679.

(T) Using the theoretical factor 0·1653.

In the system studied, specific tests for the presence of entrained precipitant in the precipitate did not seem to be available. It was assumed that, if such entrainment does take place, the addition of the solution of nitrate to the nitron acetate would provide more favourable conditions, which would result in increased entrainment, and thus affect the weight of precipitate obtained. Two authors state that the method yields somewhat high results and attribute this to such entrainment. Since the weights of precipitate obtained in the present work did not vary appreciably with the different order of mixing the solutions, it was concluded that entrainment of precipitant is not a significant factor in affecting the errors involved in the method.

Assuming now that one may disregard entrainment of cations or precipitant as a source of appreciable error, there remains the question of the general reliability of the method, including both the reproducibility of individual determinations and the actual error of results obtained with the method. It has already been stated that the results of others show considerable variation in these items. Only Gutbier and Treadwell and Hall state definitely that the results are high. In the other cases some are high, some agree well, and some are definitely low, compared with the theoretical values. The latter quantity was determined in various ways, probably not all equally dependable.*

In considering the present work, the data in Table I show, by the maximum deviations from the mean, that the reproducibility of individual determinations may be taken as quite satisfactory, particularly in view of the restrictions necessary in washing the precipitate.

Much more disturbing is the disagreement between the average value actually found for sets of determinations and the amount of nitrate calculated to be in the sample. For the different sets the latter quantity, as already indicated, was calculated on the assumption that an amount of nitrate would be present equivalent to the metal determined. For any salt that could be so handled the solution was prepared by direct weighing of the solid and then, as a check on the concentration, the metal was determined by the procedure previously mentioned. In such cases standardisation by determining the metal agreed within 0·2 per cent. with the value calculated from direct weighing. In addition, some of the salts were tested and found to conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society. Admittedly such a determination of the content of nitrate was not as satisfying as a direct method would provide. Consequently, efforts were made to obtain more direct evidence. The results in Table II include the results secured by several such methods, two of them modifications of the familiar Kjeldahl method, and the third a procedure recently proposed by Kolthoff. In the Kjeldahl procedures it seems reasonable to assume that the reduction was not complete, but no higher results could be obtained. The method of Kolthoff was not available in time to check all the solutions. Applied to a solution of potassium nitrate it yielded results averaging about the same, but not as reproducible as those obtained on the same solution by the nitron nitrate method.

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* See Hillebrand and Lundell, *loc. cit.*, p. 639, for a criticism of the method of determining nitrogen by means of a nitrometer, as used by Collins.[5]

If one makes the assumption that direct weighing of the purified salt, supplemented by gravimetric standardisation of the solution and by demonstration of conformity to specifications for purity, is sufficient evidence on which to base a calculation of the content of nitrate in the salt, then the present work indicates that in no case were appreciably high results obtained by the gravimetric determination of the nitrate. For lead, the average for all determinations was close to the calculated value; for all others, the results were low, those for copper being the lowest. If the direct volumetric determinations are taken as a more nearly correct measure of the nitrate in solution, part of the results are high, and part low, depending upon the method used in making the comparison. We are inclined to accept the first alternative. This leaves without interpretation the variation in lowness for the different salts. The chief possibilities seem to be either some error in the determination of the cation or some variation from equivalent amounts of cation and anion in the solutions. No evidence for either of these possibilities was found.

As a final point it may be mentioned that the nitron nitrate forms as a white compound in the form of relatively large crystals which are easily handled, with the exception of the necessary limitations on temperature and amount of washing. Others[24] have called attention to the advantage of using the method in certain situations. At present the cost of nitron is a definite disadvantage.

SUMMARY.—As a result of a study of the precipitation of nitron nitrate from solutions of various salts under different conditions, the following conclusions were reached:—(i) Entrainment, either of metallic cations or of precipitant, did not occur to an extent sufficient to influence appreciably the precision of analytical results.

(ii) The reproducibility of individual determinations was satisfactory, considering the solubility of the precipitate.

(iii) The reliability of the method varies for the different systems studied, if one assumes that the nitrate present is equivalent to the amount of metal found by a direct determination.

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Finger-print Detection

BY HENRY L. BROSE, M.A., D.PHIL., D.SC.

IN cases where finger-prints have been left on multi-coloured objects, such as check-patterned cigarette cases, it has been found that the ordinary photographic methods give results that are not sufficiently clear to allow the imprint to be identified or used as evidence. The back-ground comes out far more clearly than the finger-print, and it is impossible to find the twelve characteristic features of the imprint which are considered the minimum number necessary to establish identity.

A brief report of two methods devised to overcome the difficulty caused by the intrusion of the back-ground into the photographs was given in a recent issue of *Nature* (1933, **132**, 208). The purpose of the present note is to give the technical details of the processes. In the first method the details of the finger-print were isolated from the object on which it had been imprinted by dusting phosphorescent zinc sulphide powder on to the finger-print, and photographing the powder pattern after it had been rendered luminous by a source of ultra-violet light (mercury-vapour lamp, tungsten arc or carbon arc). The excess of powder between the ridges of the finger-print had to be carefully removed by gently blowing or by brushing with a soft camel's hair brush. The illumination and exposure were made to alternate with one another in the manner familiar from Becquerel's phosphoroscope. This intermittent illumination is necessary in order to separate the phosphorescent light from the ordinary visible light. If, however, a sheet of Wood's glass (obtained from Messrs. Chance Bros., Ltd.) is interposed between the source of ultra-violet light and the object bearing the finger-print, only the "dark radiation" falls on the object and excites phosphorescence. In this case it is found advisable to place a sheet of Chance's calorex glass in front of the Wood's glass to absorb the extreme red and the near infra-red rays, since the Wood's glass cracks very readily if unevenly heated. To photograph the phosphorescent finger-print it is now necessary to perform the reverse operation, that is, to eliminate all the ultra-violet light and to transmit only the visible light into the camera. This is accomplished by interposing a thick plate of Andrew's super-protex glass between the object and the camera.

It is commonly believed that the glass used for lenses of ordinary cameras transmits only light of the visible region of the spectrum. This is by no means the case. Ordinary glass does not cut off the ultra-violet light sharply, but transmits a not inconsiderable portion of the nearer ultra-violet. Super-protex glass contains a relatively high percentage of lead, and is therefore used to absorb *X*-rays. (The absorbing power of *X*-rays depends on the atomic number, and hence also on the atomic weight of the absorbent.) Investigation has shown that super-protex glass cuts off the ultra-violet light very sharply. Instead of protex glass we may use an aqueous solution of cerium ammonium nitrate contained in a rectangular cell with ordinary glass walls. It may be mentioned that the Wood's glass, referred to above, may likewise be replaced by a cell containing a solution of nitroso-dimethylaniline, but in this case the walls of the cell must be composed of quartz or of the much less expensive "vita glass." Vita glass transmits a considerable amount of ultra-violet light of the longer wave-length, and has rendered excellent service in the present investigation. A simple form of light-filter may be made by fixing a rubber ring with flat sides between two sheets of vita glass, the ring being left open at the top so as to provide an aperture through which the solution under examination or being used as a filter may be admitted. The glass walls may be clamped together by means of insulation tape tightly wound round the edges of the cell. We have used cells in which the rubber rings have had a diameter of eight inches. The "time" of exposure for these phosphorescent photographs is about twenty minutes if very fast Ilford hypersensitive panchromatic plates are used, but sharper contrasts are obtained with Ilford rapid process panchromatic plates, for which the exposure must be extended to forty minutes. The Wellington 450 plates are also very good for this purpose.

The second method of photographing finger-prints is by means of fluorescent light. In this case the illumination of the object is continuous. The arrangement of apparatus is the same as that used for continuous phosphorescence. The incident ultra-violet light passes through calorex glass and Wood's glass, and the resulting fluorescent light passes through protex glass into the camera. The accompanying figures are copies from photographs obtained with the fluorescent

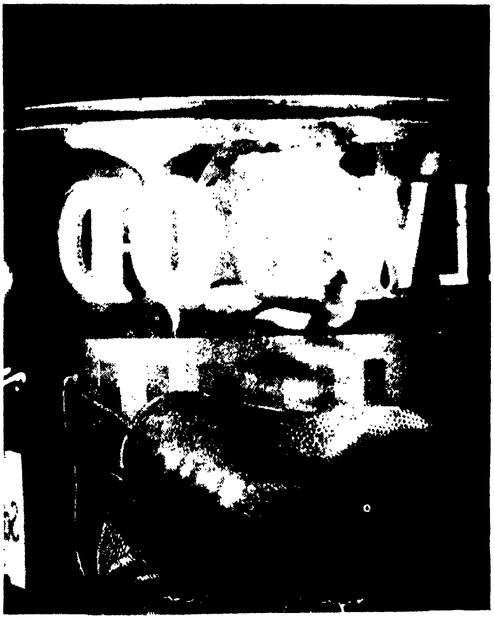


Fig. 1

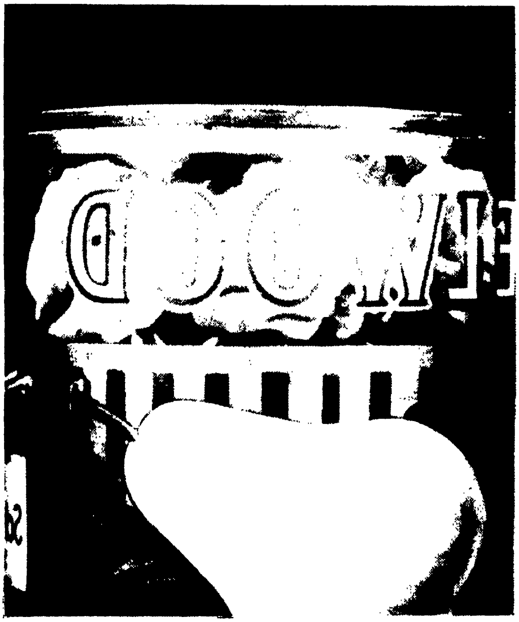
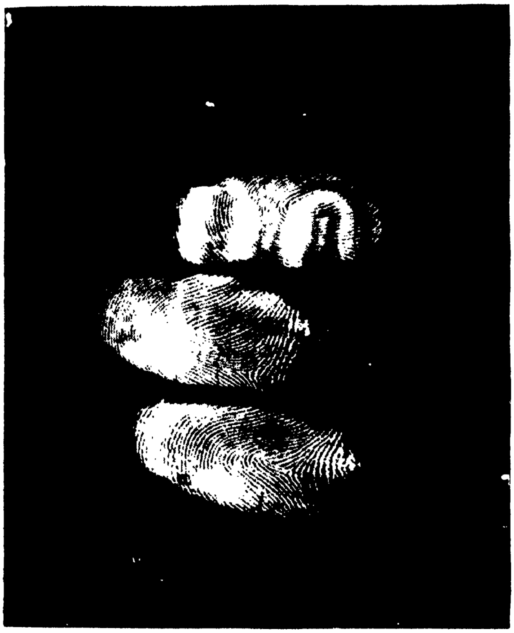


Fig. 2



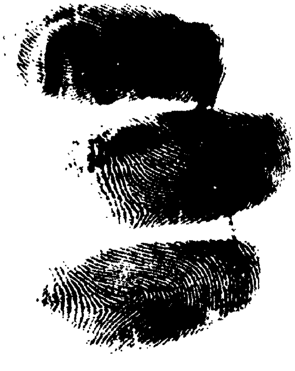


Fig. 4

Photographs of finger-prints on the multi-coloured label of a fruit tin
(Taken by members of the Derby Criminal Investigation Department)

Fig. 1. with an ordinary camera.
Fig. 2. with Wood's glass interposed.
Fig. 3. with anthracene powder dusted on to the prints.
Fig. 4. A contact print from a reversed plate (Wellington 450) with protex glass filter between object and camera. Two minutes' exposure. Stop, F.32.

method by members of the Derby C.I.D. In place of the phosphorescent powder they used very pure finely powdered anthracene. Fig. 1 represents a photograph of a finger-print taken with an ordinary camera, a Hanovia Quartz Lamp being used as the illuminant. The impress had been made on the multi-coloured label of a fruit tin. In Fig. 2 Wood's glass had been interposed between the source and the label. The finger-print has come out slightly more clearly, but not sufficiently so to admit of identification. In Fig. 3 the photograph was taken with anthracene on the ridges of the finger-print, and Fig. 4 shows a contact print made from a lantern-slide of Fig. 3. In Fig. 4 the finger-print has been almost completely isolated from the back-ground, so that the task of identification has been made extremely simple. The phosphorescence method was worked out in conjunction with members of the Nottingham C.I.D.

It is important to ensure that no light enters the camera, except that from the fluorescent or phosphorescent object; this may be achieved by using a light-tight conical funnel blackened on the inside. Both the camera and the ultra-violet light source must be carefully screened. The technique described above may, of course, be used for the photography of any fluorescent object whatsoever, and the use of the glasses and photographic plates mentioned will be found to enable good photographs to be obtained with time of exposure much less than is usual (often many hours) when other materials are used. The interposition of calorex glass allows the source of light to be brought much nearer to the object than when Wood's glass is used alone; this again reduces the time of exposure.

University College
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Notes

The Editor wishes to point out that the pages of the Journal are open for the inclusion of short notes dealing with analytical practice and kindred matters. Such notes are submitted to the Publication Committee in the usual manner.

THE COMPOSITION AND CALORIFIC VALUE OF ENGLISH CIDER

Two kinds of cider can be differentiated and characterised:

I. Sharp Ciders (*Cidres de pommes aigres. Apfelwein*).—In the fruit mixture sharp apples must preponderate. The juice is pale and thin, being low in tannin, but high in acidity and total nitrogen. The fermentation is rapid, rather tumultuous, and complete; the sugar disappears before the nitrogen is exhausted. The ciders are not naturally sweet, but they can be made sweet. A great loss of titratable acidity occurs during manufacture (Säureabbau; désacidification). The juice from the press has from 0·7 to 1·5 per cent. of acidity (calculated as tartaric acid), and half of this may be lost, malic acid being equimolecularly transformed into lactic acid. Ciders A to F in the following table are sharp ciders, ranging from a sparkling apple wine to a still, diabetic cider. The first had 465 calories per pint, and the specially dry cider had 275, thus being equal to stout in food value. The manufacture of sharp cider provides an alternative market for the grower of table and culinary apples.

II. West-country Cider (*Cidres naturellement doux, sucrés par fermentation alcoolique incomplète*).—The fruit must include a suitable proportion of bitter-sweet, sharp, and sweet cider apples. The juice is coloured and darkens on contact with oxygen or alkali. The sp.gr., sugar, tannin and pectin are high, whilst the nitrogen and acidity (below 0·7 per cent.) are low. The fermentation is slow and incomplete, throwing up a brown head and depositing calcium pectate (*fermentation pectique*). Extraction of the juice by diffusion inevitably introduces some 20 per cent. of water. The composition and calorific values of G and H are typical. Chapman (1932) gives 275 calories for bottled cider and 228 for draught cider. Cider apples are useless for anything except cider-making.

The extract or total solids of cider includes mineral matter, sugar, tannin, pectin, glycerol, sorbitol, and organic acids, some of which have a doubtful *net* energy value. For the present purpose, however, the calorific value is taken to be: Calories, per pint = (extract per cent. × 22·4) + (alcohol Vol. per cent. × 32.0).

	A	B	C	D	E	F	G	H
Sp.gr.	1·0114	1·0222	1·0253	1·0098	1·0189	0·9979	1·0194	1·0218
Original gravity	1·0868	1·0784	1·0701	1·0677	1·0592	1·0529	1·0537	1·0395
Acidity (tartaric)	0·78	0·83	0·61	0·59	0·59	0·56	0·45	0·38
Alcohol (by vol.)	10·03	7·36	5·79	7·60	5·21	7·16	4·36	2·30
Extract ..	6·42	8·40	8·66	5·25	6·82	2·05	6·70	6·44
Sugars	4·12	6·16	6·91	3·17	5·32	0·12	5·13	5·35
Non-sugars ..	2·30	2·24	1·75	2·08	1·50	1·93	1·57	1·09
Ash	0·23	0·21	0·17	0·23	0·13	0·22	0·23	0·13
Calorific value ..	465	423	379	361	319	275	290	218*

* Saccharin present.

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THE DETERMINATION OF CARBON IN GRAPHITED CUP GREASES

I was recently asked to determine the amount of carbon in samples of graphited cup greases and to report on the quality of the carbon. The specification required that the greases should consist of a lime soap base with the addition of 5 per cent. of graphitic carbon. It was, therefore, necessary not only to determine the free carbon, but to isolate it in an unchanged form for further examination. The following method was found to be very satisfactory:

From 3 to 4 grms. of the sample are weighed into a small beaker, 30 to 40 ml. of glacial acetic acid are added, and the mixture is gently boiled for a few minutes. During this operation the lime soap base is first dispersed in the acetic acid in the form of small liquid globules, and subsequently dissolves completely, being decomposed into calcium acetate and higher fatty acids.

The mixture is filtered, with the aid of slight suction, through a weighed Jena-glass crucible with sintered glass disc of suitable porosity. The residue of carbon in the crucible is washed two or three times with hot glacial acetic acid, and then thoroughly with hot water, after which the crucible and contents are dried and weighed.

The above method is quick and reliable; a perfectly sharp separation is achieved, and the carbon can be further examined if required.

The disc of the crucible can be cleaned afterwards by the prolonged action of hot fuming nitric acid, to which a little potassium chlorate has been added, followed by extraction with dilute solution of alkali and washing.

F. HEATHCOAT

DEPT. OF METALLURGY AND INDUSTRIAL CHEMISTRY
COLLEGE OF TECHNOLOGY
ROTHERHAM

AN AID TO THE READING OF GERBER MILK-FAT TUBES

OWING to the transparency of the fat separated in the Gerber method of determination, the reading of a large number of tubes in artificial light, or even in daylight, is tiring, especially when the graduations on the tubes are not widely separated. The meniscus is made more visible by the following device:

A light-tight box, of height greater than the length of a Gerber tube, and width not less than three inches, has one face removed and replaced by a sheet of glass, the inner side of which is completely covered by grease-proof paper. Inside the box an ordinary electric filament lamp is placed and connected with a plug or switch. The box is then fixed to the wall at a convenient height, forming a translucent window. The Gerber tube is held at a distance of about one inch from the glass, against which both the zero line and the upper meniscus of the fat layer stand out clearly. We have not tried ground-glass in place of the paper-covered glass but, no doubt, this would give equally good results.

E. B. GRAYSON

CITY ANALYST'S LABORATORY
SHEFFIELD

FREEZING-POINT OF MILK—HORTVET METHOD

I WISH to point out an omission in the instructions given in the *Methods of Analysis of the A.O.A.C.*, which I think might be worth recording in THE ANALYST.

No mention is made of the necessity of removing the freezing starter from the apparatus before tapping the thermometer, proof of which is shown in the following experiment. On one occasion the starter was accidentally left in while the zero was being determined, and a zero of +0·040° C. was obtained, as against +0·022°C. To test whether the starter had anything to do with the former figure, several determinations of the zero were made, with and without removal of the starter. When the starter was removed a constant zero of +0·022° C. was obtained, but when it was left in, the zero varied between +0·022° C. and +0·040° C. After a constant zero of +0·022° C. had been obtained, the starter, which had been kept in ice, was again inserted, and the thermometer tapped; the zero jumped up to +0·038° C. In every instance when the zero jumped, there was a distinct click, as though the starter had hit the thermometer during tapping. The above experiment has also been tried on samples of milk and with similar results.

ERNEST V. JONES

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COUNTY BUILDINGS, STAFFORD

Official Appointments

The Minister of Health has approved the following appointments:

Frederick William Edwards as Public Analyst for the Metropolitan Borough of Westminster (City of), in place of P. A. Ellis Richards, resigned December 31st, 1933 (December 23rd, 1933).

Albert Houlbrooke as a Public Analyst for the County Borough of Leeds, in addition to C. H. Manley (December 23rd, 1933).

Erratum:—January issue, p. 29: *For* "F. G. D. Chambers" *read* "F. G. D. Chalmers as Additional Public Analyst for Coventry.

Notes from the Reports of Public Analysts

The Editor would be glad to receive the Annual or other Reports of Public Analysts containing matter of special interest to the Society. Notes made from such Reports would be submitted to the Publication Committee.

CITY OF BIRMINGHAM

Report of the City Analyst for the Third Quarter, 1933

Of the 1193 samples of food and drugs examined during the quarter, 11 were bought formally and 1182 informally. The total number returned as adulterated or incorrect was 65.

Tea "Free from Tannin."—A sample was labelled as being composed only of the tips of the leaves and therefore free from tannin. Analysis showed it to contain 14·1 per cent. of tannin. The packers agreed to amend their description, and circulars to this effect were sent to their customers.

Liquid Paraffin.—A sample of liquid paraffin was not of the correct viscosity, the figure being 237 seconds, as against the minimum B.P. figure of 260 seconds. The sample was examined by the supplying firm, and they agreed that it was not of B.P. quality, and replaced the liquid paraffin remaining in stock by a new supply of the correct viscosity.

H. H. Bagnall

BRISTOL

Report of the Public Analyst for the Year 1932

Sixty-six of the 1400 samples of foods and drugs examined were adulterated.

Tea.—Seventeen samples gave the following mean analytical results: Total ash, 5·67; soluble ash, 3·44; alkalinity (as K_2O), 1·65 per cent. There was no evidence of spent leaves or foreign structures, but two samples contained excess of stalk and gave soluble ash, 2·7; and alkalinity, 1·3 per cent.

Preservative in Walnuts.—Three samples of walnuts containing sulphurous acid were condemned, the amounts being 0·12, 0·04 and 0·01 per cent.

Port Samples.—One hundred and sixty-nine samples were examined, including dried fruits, fruit pulps, etc., mainly for the presence of preservative. A sample of raisins alleged to be damaged contained 0·14 per cent. of combined chlorine, thus showing slight but definite evidence of contamination. Samples of white haricot beans and rice, alleged to be damaged, contained fungal hyphae, and the washings from the beans also contained excess of chlorine.

Arsenical Contamination of Frozen Meat.—Frozen liquid from cloth off two lambs' carcases contained 0·0004 and 0·004 per cent. of arsenious oxide, and a sample of frozen liquid and meat contained 0·0028 per cent. Thirteen other samples of meat, cloth or ice, suspected of containing arsenic, gave a negative result or contained mere traces in 5 cases; the remaining 8 samples gave amounts ranging from 0·00003 to 0·0025 per cent. of arsenious oxide.

An investigation was made by the Medical Officer of Health to discover the origin of the contamination. The carcases affected were for the most part in two tiers in the hold of the ship, and above them there was evidence of a leak in the deck having taken place. Samples of pelts and of pelt liquor which had been discharged at London from that deck were examined, but it was concluded that they were not the source of the arsenic. Every other effort to trace the origin of the contamination was unsuccessful.

Gas in Tinned Cherries.—Samples of cans of cherries having a blown appearance were opened by sterile puncture, and inoculation made into broth tubes; in every instance, except one, the contents were sterile, and had an agreeable taste. Gas collected from two of the tins measured 25 ml., and proved to be hydrogen. The interiors of the tins were slightly excoriated, but there was only 0·01 per cent. of tin in solution, or about half the amount corresponding with the hydrogen present. It was concluded that the cherries were perfectly sound.

EDWARD RUSSELL

LEICESTER

ANNUAL REPORT OF THE CITY ANALYST FOR 1932

THE number of samples examined was 2386, of which 1472 were of food and drugs. These included 900 milk samples and 43 of these were reported "not genuine."

ALKALINE LARD.—A sample, which was alkaline in reaction and yielded 0·13 per cent. of ash consisting of sodium carbonate, was condemned. It was not clear whether the alkali had been deliberately added to mask acidity, or whether its presence was accidental from a previous washing process.

POTTED MEAT.—Of 36 samples examined, 3 contained starchy matter equivalent to 8·8, 5·1 and 6·8 per cent. of dry starch, respectively. There is no provision in the Public Health (Preservatives, etc., in Food) Regulations for any cooked meat to contain preservative. Two of the samples containing starch also contained sulphur dioxide (162 and 135 parts per million). The maker had used a preservative preparation intended for use only with sausage meat.

One sample contained 28 parts of sulphur dioxide per million, but the maker emphatically denied that he had used any preservative, and submitted a further sample for examination. This was found to contain 9 parts of sulphur dioxide per million. Ten days later, when the sample was in a decomposing condition, the apparent sulphur dioxide content had risen to 55 parts per million. The inference was that the sample was exhibiting incipient decomposition, although no other indications of this had been observed. Potted beef, when made from corned beef, tends to give off traces of volatile sulphur compounds under the usual conditions of determination.

CELERY PILLS.—Samples were accompanied by a formula giving the composition of each pill, one item in which was "Phenolphthalein . . . gr. ⅛." Analysis showed that none of this ingredient (the most expensive in the formula) was present. The manufacturer was cautioned.

Many compound drugs are now sold with the composition declared, the object being to avoid paying Stamp Duty, since no proprietary rights are claimed. In the case of such products, there seems good scope for sampling, since there can be no question of the fairness of judging an article by a standard volunteered by the manufacturer; however, the onus should be on the manufacturer and not on the retailer.

BATH WATERS.—The great amount of bacterial pollution which may occur in swimming baths has long been recognised, and continuous treatment is necessary to maintain the water in a safe condition. The most effective agent for this purpose is chlorine, following the processes of filtration and aeration.

One can only be sure of the safety of the water by making regular bacteriological examination; the treatment can then be adjusted accordingly. About one part of chlorine per million is the optimum amount. A certain threshold value is necessary to oxidise organic matter, nitrites, etc., before the residual chlorine has any bactericidal effect, while amounts much in excess of one part per million become self-evident and objectionable to bathers.

After some preliminary tests, the following standards were adopted, and regular sampling was carried out throughout the year.

Standards.—(i) The free chlorine shall not exceed 0·5 part per million. (ii) The bacterial count (24 hours on agar at blood heat) shall not exceed 1000 organisms per c.c.; (iii) *Bacillus coli* shall not be present in more than two out of five 10 c.c. tubes.

System of Sampling.—Each bath is sampled the first week it is open to the public for the year. If the water fails in any one of the above tests it is sampled again weekly until a satisfactory sample is obtained. It is then sampled again after a fortnight, and, if still satisfactory it is sampled thereafter once a month.

If the first sample from a bath is satisfactory it is sampled again after a fortnight, and thereafter monthly while it remains satisfactory.

Generally speaking, it has been found that so long as the water gives a good reaction for free chlorine the bacterial results are satisfactory, and *vice-versa.*

F. C. BULLOCK

Legal Notes

Under this heading will be published notes on cases in which points of special legal or chemical interest arise. The Editor would be glad to receive particulars of such cases.

MINT ADULTERATED WITH AILANTHUS LEAVES

On November 27th three shopkeepers were summoned at Sheffield Police Court for selling packets of dried mint adulterated with ailanthus leaves in proportions ranging from 15 to 20 per cent.

Mr. John Evans, F.I.C., the City Analyst, said that the foreign leaves in the sample of dried mint examined by him were leaves of the ailanthus, or "tree of heaven" (*A. glandulosa*), a Chinese tree which had been acclimatised in Europe.* They did not possess the properties of mint, or of sage, marjoram or thyme, which belonged to the same order of herbs as mint. They were quite useless, and were not accidental impurities.

For the defence it was urged that technical and unavoidable offences had been committed. The mint in question was a blend of British and foreign mint leaf, and the foreign constituents had been adulterated before it reached this country. The mint had been supplied to the respective defendants in packets and had been sold in the same form. The London wholesalers, who had supplied the mint to one of the defendants, had heard of the adulteration earlier in the year, and, acting on the representation of the Ministry of Health, had attempted to get back all supplies; they had, in fact, recovered 309 lbs. of mint, representing from 6000 to 7000 packets, and it was extraordinarily unfortunate that the inspector should have got some of the packets that had not been returned.

Fines of 5s. and costs were imposed in each of the three cases.

A firm of Sheffield manufacturing chemists was then charged with "consigning certain food, to wit, dried mint, which was not of the nature, substance and quality demanded by the consignee, and contained foreign leaf."

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* Structure of Ailanthus Leaves.—The accompanying diagrams and description of the microscopic structure of *Ailanthus* leaves are reproduced by permission of Messrs. G. Stafford Allen and H. Deane from their communication to the British Pharmaceutical Conference, 1914 (*Year Book of Pharmacy*, 1914, p. 337). Calcium oxalate crystals are distributed in lines along the veins, in some leaves occurring even in the smallest branches. Fig. I is an intermediate example. The epidermal cells are polygonal, and stomata occur only on the lower surface (Fig. II). The striations on the upper surface usually radiate from the hairs. These are characteristic, being slightly curved, unicellular, and usually thick, though occasionally thin-walled. Sometimes they attain a great length; the hair represented in Fig. III is rather short. The leaves were for a long time used as a substitute for sumach, which they resemble, but it was shown by A. G. Perkin (*J. Chem. Soc.*, 1898, 73, 383) that they are valueless as a tanning agent. According to Mitlacher (*Z. allgem. Oest. Ap. Ver.*, 1911, 49, 149) *Ailanthus* leaves were being used in 1911 in Italy as an adulterant of senna and of belladonna.

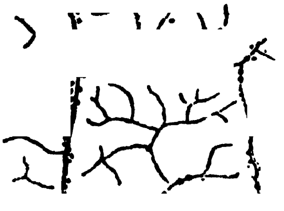

Fig. I. ×27.

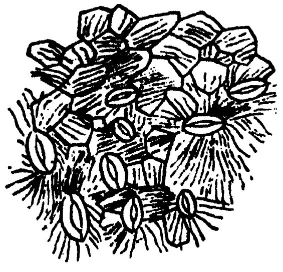

Fig. II. ×135.

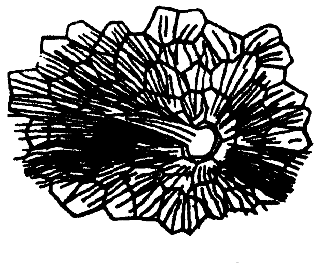

Fig. III. ×135.

Mr. John Evans said that the sample in question contained not less than 12 per cent. of ailanthus leaves. He did not think that its therapeutic action had been worked out, but agreed that, so far as he knew, ailanthus was perfectly harmless. He would consider that he was prejudiced if he received mint sauce or savoury stuffing containing ailanthus, just as much as he would be if he received stuffing containing sawdust, which was also inert from the therapeutic point of view.

Mr. Okell submitted that there was no case for the defendants to answer, since the section of the Act under which the summons had been issued related to the purchase of goods from a retailer. The defendants were wholesalers, and, in his submission, there was no case against the wholesaler. The Act dealt in the first place with the person who originally mixed the herb. The firm was summoned as consignors, and he submitted that that form of summons did not allege an offence, but that the summons had been concocted under another section of the Act, which provided that the sampling officer might, when the retailer was delivering goods to the purchaser, take a sample at the place of delivery. The summons was formed under that section, but that section did not specify any offence; it simply described the powers of the sampling officer.

There could be no doubt that his clients were innocent victims who had been badly let down by their foreign supplier.

A fine of £20 and costs was imposed.

Mr. Okell said that notice of appeal would be given.

Department of Scientific and Industrial Research

REPORT OF THE FUEL RESEARCH BOARD FOR THE YEAR ENDED MARCH 31st, 1933*

THE Report opens with a summary of the main investigations in progress at the Fuel Research Station and in the Survey Laboratories, and is followed by the more detailed report of the Director of Fuel Research, which is divided into an Introductory Section and nine other sections.

PHYSICAL AND CHEMICAL SURVEY OF THE NATIONAL COAL RESOURCES.—Survey committees are now at work with the co-operation of the mine owners and the Geological Survey in nine coal areas covering 96 per cent. of the present production of the country. Outlines of the results in the various areas are given, and reference is made to Survey Papers, Nos. 19 to 27.

EXAMINATION OF COAL AND COKE.—*Microscopical Examination of Coal.*—Mr. C. A. Seyler has continued his study of methods for the investigation of the micro-structure of coal. During the year, attention has been paid chiefly to the percentage of light reflected from polished surfaces by the various micro-petrological constituents of coal, a Berek slit photometer being used for the purpose. The brightness of the components is related to the "rank" (*i.e.* degree of coalification) or composition of the coal. As a rule, the brightness of the vitrain component increases with the rank, whilst the spore material is much less reflective than the vitrain in bituminous coal, but is nearly as bright as the vitrain in anthracite coal.

Significance of Spores in the Correlation of Coal Seams.—This has been dealt with in Survey Papers No. 17 and No. 23. It has been inferred that, in the absence of a characteristic spore, the microscopical method of correlation is only applicable where a full thickness of seam is available, and thin sections can be prepared, inch by inch. But if a fair sample of the seam is available, even though it be crushed, the spore examination may still provide useful data, for if the numbers of individual spore types are recorded as a percentage of the total number of spores counted, percentages of similar magnitude are found in different sections of the same seam.

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* H.M. Stationery Office, Kingsway, W.C.2. pp. 135. Price 2/6 net.

Examination of certain Durains and Clarains.—It has been found possible, by a method of gravity separation, to separate the durain of the Plessey seam of Northumberland into a number of fractions which show a progressive change of hydrogen-content. The fractions contain different amounts of spores, the highest spore-content being associated with the highest hydrogen-content and the lowest specific gravity.

CONSTITUTION OF COAL.—*Oxidation of Coal and Allied Substances.*—The work of Professor Bone at the Imperial College has been mainly concerned with a systematic examination of the alkaline permanganate oxidation of representative celluloses, lignins, peats, brown coals, bituminous coals and anthracites. So far the results indicate that the matured coal substance has mainly originated from lignin.

Action of Solvents on Coal.—The report on this part of the subject has been published in *Technical Paper* No. 37.

ANALYSIS OF COAL.—*Volatile Matter.*—The British Standards Specification (No. 420, 1931) suggests that the temperature at which the volatile matter test is carried out should be so adjusted that crystals of potassium chromate show incipient fusion when placed in the bottom of the crucible. Pure potassium chromate melts at 965° C., whereas the normal temperature for the test is 925° C. Attempts have been made to use other salts in the test, but each contained sufficient impurity to influence the test. Hence the thermo-couple method seems to be the most satisfactory for the purpose.

Nitrogen.—Experiments on the lines of Börnstein and Petrick (*Brennst. Chem.*, 1932, **13**, 41) have shown that the nitrogen loss in the Kjeldahl process is only about 0·04 per cent., after the occluded nitrogen has been drawn off.

Coal Ash.—A scheme, based on methods already recognised for the analysis of silicate rocks, has been published in Survey Paper No. 28 (*cf.* ANALYST, **1933**, **58**, **614**). Spectroscopic methods are being applied at the National Physical Laboratory.

Phosphorus.—A new method of determining phosphorus in coal ash has been worked out in detail; it involves the precipitation of the phosphorus as magnesium ammonium phosphate, without removal of the metals of the iron group. Citric acid is added to a solution of the ash, and the resulting complex salts of iron, aluminium and titanium remain in solution throughout the analysis. This avoids the necessity for repeated fusion and extraction of insoluble residues; apparently the inhibiting influence of certain elements on the precipitation of the phosphorus is also checked.

Vitrain containing Titanium.—Samples of exceptionally pure vitrain obtained from fossilised tree trunks, known locally as "cauldron bottoms," have been examined in the Coal Survey Laboratory at Newcastle. The ash from the cleaned coal has been found to contain titanium (approx. 15 per cent.).

Chlorine in Coal.—Tentative methods for the determination of total and water-soluble chlorides have been evolved. These methods were used for the investigation of the horizontal and vertical distribution of chlorine in two N. Staffordshire coal seams.

The vertical distribution of total chlorine and the proportion of water-soluble to total chlorides were found to be approximately constant, but there were considerable variations in the horizontal distribution, the total chlorine in the seams varying from 0·02 to 0·66 per cent., and the water-soluble chlorides from 0·01 to 0·46 per cent. in different parts of the field. As a general rule, the chlorine-contents of the dirt bands, the floor and roof strata and other non-coal materials were substantially lower than those of the associated coal. Washing processes removed only a small proportion of the water-soluble chlorides, and actually increased the percentage of both forms of chlorine by removing the strata, etc., containing the lower percentage of chlorine.

In commercial grades of the coals the chlorine was found to be concentrated to some extent in the fine grades. Removal of the finest grades of the slack slightly reduced the chlorine-content, but experimental work suggested that a steaming process at a temperature above 200° C. is probably the only method by which the chlorine-content of a coal could be appreciably reduced on a commercial scale.

Calorimeter Bombs.—Experiments with a certain stainless steel bomb showed that the steel was acted upon by the acids formed during combustion. Further search, and tests on several makes of British stainless steel, showed that two of these were suitable for this purpose, the action on the metal being very small. As an experiment the first-mentioned bomb was chromium-plated inside, and tests were carried out which showed that no chromium, and only a trace of iron, was present after several hours' exposure to acids. This bomb has now been used for about 500 determinations of calorific values, and the chromium plating appears to be still in good condition. Some further corrosion tests were made, and these showed no traces of either chromium or iron in solution. A monel metal bomb in which corrosion occurred has been similarly treated, with quite satisfactory results.

Errors of Sampling.—Parallel series of 64 determinations on laboratory samples of coal and on pure chemicals were made. The results have been analysed in accordance with the Law of Errors, and are being published as Survey Paper No. 29.

Reduction of Coal Samples for Analysis.—A simple type of sampler has been designed, constructed, and tested at the Fuel Research Station, and has been found to give satisfactory results, with a great saving of time and labour as compared with the usual method of "coning and quartering."

The apparatus consists of two concentric metal cones mounted together so as to enclose an annular space between them. On the outer surface of the inner cone two chutes are fixed diametrically opposite to one another, extending from a position near the base of the cone, and terminating at their lower ends in the sample offtakes. The top of the outer cone terminates in a short length of parallel tube, above which is fitted a special slide valve and hopper. The apex of the inner cone projects inside the short length of straight tube.

The gross sample of coal to be reduced is charged to the hopper, a slide at the base of the latter is withdrawn, and the coal flows in a solid column down the tube and streams over the apex of the inner cone. Two sections of the annular stream of coal flow into the chutes and are discharged through the sample offtakes. The remainder of the coal, or reject portion, is discharged at a central offtake.

The portions of the coal discharged from the sample offtakes are taken together to form the sample, further reduction of which may be done either in a smaller "cone" sampler or in a riffle.

Softening Points and Coking Properties of Coal.—Work by Mr. C. A. Seyler has been continued (*cf.* C. A. Seyler, Presidential Address, *Proc. South Wales Inst. of Engineers*, 1931). A precise definition of the "softening points" of coal and their relation to the plasticity has been formulated, and a practical method of determination of the plasticity at different temperatures, based upon the softening point under different loads, has been devised.

Structure and Reactivity of Coke.—An investigation on the structure and reactivity of coke has been carried out by Professor J. W. Cobb at Leeds University, and a resumé of his results is given in the Report (pp. 40–42).

CLEANING and DE-ASHING OF COAL AND ITS PREPARATION FOR THE MARKET.—Experiments have continued on the cleaning of coal by the vacuum-flotation process and on the improvement of slurry settling tanks. A new process for the dry cleaning of coal designed in the South Yorkshire Coal Survey Laboratory is under investigation, and shows considerable promise.

CARBONISATION OF COAL.—Experiments on increasing the velocity of the heating gases in horizontal retorts have been continued, and show the advantages and limitations of this method of increasing the throughput of the retorts. An investigation of the possibility of increasing the yield of gas in horizontal retorts by steaming is in progress.

The new setting of vertical chamber ovens was completed and put to work in November, 1932; it will be used for experiments on the effect of blending coals on the coke, tar and gas produced.

The new setting of narrow vertical brick retorts, intended for use at lower temperatures than those normally used in gasworks to produce a free-burning coke and tar suitable for hydrogenation, has been at work since April, 1931. Experiments indicate that this design of retort may be suitable for use over a wide range of temperatures.

USE OF PULVERISED COAL, INCLUDING MIXTURES OF COAL AND OIL ("COLLOIDAL" FUEL).—The "Grid" burner designed at the Fuel Research Station has given promising results, and is being developed.

Progress has been made with the problem of stabilising dispersions of coal in oil.

HYDROGENATION OF TAR AND COAL.—Experiments have shown that the ease of hydrogenation of tar varies rapidly with the temperature of carbonisation over a critical range. Much of the plant of the larger shale unit has been erected, and experience with a unit dealing with 100 pounds of tar a day is being applied to the design of a unit with a daily throughput of one or two tons.

MISCELLANEOUS.—Other subjects dealt with in the Report include internal combustion engines, domestic heating, a description of a new lamp for the determination of sulphur in light spirits, an apparatus for the removal of fog from gases, and heat losses from surfaces.

There are three appendices: I, List of Fuel Research Staff; II, List of Committees and their Members; III, List of Publications, (*a*) official; and (*b*) other publications since March 31st, 1932, containing reports on work connected with the Board. The Index occupies four pages.

Government of Madras

REPORT OF THE CHEMICAL EXAMINER FOR THE YEAR 1932

THE Chemical Examiner (Lt.-Col. Clive Newcomb, F.I.C.) reports that there was a small decrease in the cases and articles received for examination in 1932 (6136 articles as against 6360 in 1931).

HUMAN POISONING CASES.—Opium again heads the list as the poison of most frequent occurrence (33 cases), arsenic coming next (24 cases), then mercury (18 cases) and oleander (16 cases). Unidentifiable poisons were found in 12 cases; this shows the need for research on the indigenous vegetable poisons, so that suitable tests for identifying them may be found. The total number of poisoning cases investigated was 323, and in 168 of these poison was found.

Madar Juice Poisoning.—There were 7 cases of poisoning with the white juice of the poisonous weed, madar (*Calotropis gigantea*), which is commonly used as a poison by the mouth or as an abortifacient introduced into the uterus on a small stick. In addition to the identification tests previously described (ANALYST, 1931, **56**, 665), the following new test has been devised:—An alcoholic extract of the juice, when hydrolysed with caustic potash and extracted with petroleum spirit, yielded a large amount of a white crystalline substance readily soluble in ether and chloroform. This substance gives a crimson colour with sulphuric acid. Even in the presence of fats, as in the examination of viscera, it can be readily extracted in cases of madar poisoning.

Poisoning with Oduvan Leaves.—The acidified ethereal extract of the leaves gives a green colour with strong hydrochloric acid and a purple colour with strong sulphuric acid, and causes paralysis and death when injected under the skin of a frog. The green colour with hydrochloric acid, however, often cannot be obtained with extracts of viscera, although the other reactions are obtainable. The oduvan leaf has the following microscopic characteristics: (i) an upper epidermis of polygonal cells with no stomata; (ii) a single layer of palisade cells; (iii) a spongy mesophyll with large prismatic crystals of calcium oxalate in abundance along the course of both sides of the vessels; (iv) a lower epidermis of wavy-walled cells with numerous stomata. The stomata are surrounded by two cells, each of which is parallel to the ostiole (*cf.* ANALYST, 1931, **56**, 665; 1932, **57**, 717). The root of this plant is also poisonous.

Oleander Poisoning.—Yellow oleander is one of the most commonly used poisons in Madras, the red variety being much less frequently used. Both varieties, when extracted with acidified ether, yield extracts fatal to frogs and giving a deep violet colour with sulphuric acid after the lapse of several hours. The fresh kernels of the yellow variety give a green colour when boiled with hydrochloric acid, but this reaction is not obtained with viscera. In an investigation of the poisonous constituent, Dr. R. Naydu has obtained the following results:—The expressed seed cake was extracted with a mixture of chloroform and ether (1: 2), and the extract was evaporated to dryness, freed from oil by means of petroleum spirit, and dried (Extract A). The kernels were next extracted with absolute alcohol, the extract was treated with ether, and the resulting precipitate was purified by re-precipitation and dried (Extract B). Extract A had an ultimate composition agreeing with that of thevetin. It gave a cherry-red and then violet colour with concentrated sulphuric acid, and, when painted in dilute solution on a frog's heart produced characteristic effects. Extract B was very poisonous when injected into frogs (vomiting, paralysis, asphyxial spasms and death), but was comparatively non-toxic to white rats. For guinea-pigs the minimum lethal dose was 10 mgrms. per kilo. of body weight. This extract gave a deep blue colour when boiled with dilute hydrochloric acid.

Eucalyptus Oil.—In two cases of suspected eucalyptus oil poisoning, in each of which about an ounce of the oil was drunk, eucalyptus oil was detected in the vomit. At the trial, medical evidence was given that eucalyptus oil was not ordinarily likely to cause death, and, on this evidence, the accused were acquitted of the charge of a mutual suicide pact. The doctor's opinion, that eucalyptus oil is non-poisonous, is generally accepted, though it is questionable whether it is correct. The comparative harmlessness of the eucalyptus oil ordinarily bought in the Madras bazaars may be due to its being heavily adulterated with other oil—probably arachis oil.

Betel Poisoning.—Cases of poisoning by chewing pan supari are reported from time to time. The substance chewed consists of betel leaves wrapped round areca nut and slaked lime. Which constituent is the occasionally poisonous one is uncertain. In a case sent in during the year under report a man, aged about 30, after chewing a roll of betel leaves began to sweat profusely and suffered from vomiting and diarrhoea. His symptoms rapidly got worse and he went into convulsions, became unconscious, and died within an hour. As is usual in such cases, no poison could be detected in the viscera. An investigation of the alkaloids of areca nut is in progress, with a view to discovering which of them may give rise to these symptoms.

INCENDIARISM IN MADRAS.—There were several cases of incendiarism during the year, and in every instance yellow phosphorus was probably used. In one house the bedding of the horses in the stables, a cloth over a tea tray, a towel over a cane chair, and several other articles were observed to be smouldering at different hours of day and night without any apparent cause. These strange happenings were attributed to black magic; but, as portions of the burnt articles all revealed traces of phosphoric acid, it is more probable that phosphorus (possibly in solution) and normal human spite were the cause of the phenomena.

There have been several attempts to set fire to the contents of postal letter boxes. In some cases yellow phosphorus was found rolled up in a moist cloth; and, in others, in which the articles were partly burnt, phosphoric acid was detected in the charred portions. In one of these attempts at arson a child's toy clockwork motor car had been used to convey the incendiary material through a hole too small for any larger apparatus.

IDENTIFICATION OF TYPEWRITERS.—An investigation was made in connection with certain anonymous typewritten letters to ascertain if it is possible to determine whether two specimens of typewriting, each typed on a new machine of the same make, with none of the letters distorted and with good alignment, originated from the same or from different machines. The problem is more difficult than in a case in which there are obvious defects in the face of the type; these settle the matter at once; there is, however, always the possibility that the writer of incriminating documents may have the cunning to use a new machine in good condition for typing them. The tests showed that, however good the machine, each letter has its own mean alignment, although the differences may be imperceptible to ordinary observation. This characteristic was found to be a more useful measurement than the spacing between the letters, which may vary according to the position of the letter in the typescript, the speed of typing, etc.

The procedure adopted was as follows:—A straight line is ruled just below the lines of type and the distance from the top of this line to the bottoms of the various letters is measured. Several measurements of the same letters (E, T, A, O, I, N, S, R, H) are made by means of a travelling microscope giving a magnification of about 25 diam., and having a vernier reading to 0·02 mm. From the measurements obtained for a given line the straight line which, as nearly as possible, touches the bottom of all the letters, is calculated (by the method described in any book on the theory of statistics), and the measured alignments of the letters are then adjusted as from this line. Then, after 200 to 300 letters in each specimen of typescript have been calculated, the mean alignment of each of the selected nine letters and the deviation of the letter about this alignment are calculated.

If it is found that the mean alignments of some of the letters differ in the two specimens of typescript by more than can be accounted for by the chance deviations in alignment, the specimens have been typed on different machines. If, on the other hand, the mean alignments of all the letters are within the allowable deviations, it is probable that the two specimens were typed on the same machine, but here it is more difficult to estimate the probability of this conclusion. Data are needed as to the variations in the alignment of the letters on different machines of the same model.

It should be borne in mind that on an old machine the deviations of the various impressions of some letter may be large, some being visibly out of alignment upwards and others downwards. A hasty conclusion from the naked eye observations of a few impressions of this letter might easily lead to error.

New Zealand

ANNUAL REPORT OF THE CHIEF CHEMIST, DEPARTMENT OF AGRICULTURE

THE Report of the Chief Chemist (Mr. B. C. Aston, F.I.C.), of the Department of Agriculture, is published as a section of the Annual Report of the Department. In addition to details of analyses of soils, fertilisers, etc., the Report gives particulars of certain special investigations.

USE OF LIMONITE IN "BUSH SICKNESS."—Perhaps the most remarkable and far-reaching aspect of animal nutrition ever experienced in the Dominion's history has been brought about by the widespread adoption of the advice given by the Chief Chemist in the use of limonite for the rectification of those stock conditions associated with iron deficiency and generally known as "bush sickness." The use of finely ground high-grade limonite can now be looked upon as a standard farm practice on all known bush-sick country, and is rapidly extending to the marginal areas where the condition is present in a modified form. The treatment is so well recognised that the distribution of the material has been taken up by commercial agencies, some operating on an extensive scale. Successful treatment of iron deficiency by such simple means is proving a godsend to farmers in affected country.

Air-deposited rhyolite pumice, which is the type of volcanic ash associated with bush sickness in the North Island, constitutes the chief soil-forming material over an area of about 8,000 square miles, or one-fifth of the total area of the North Island. Bush sickness has so far been found to occur over about half of this area, or more than two and a half million acres. Within the outer boundaries of this proved sick area, however, scattered portions, associated mainly with special topographical features, are relatively healthy. The occurrence of various degrees of pathogenicity is well established, and it is probable that much of the remaining subaerial-pumice country, on large areas of which stock-farming with modern methods has never been attempted, will be found eventually to be affected with bush sickness, either in the usual condition or to the extent that treatment with iron licks, such as limonite, will materially increase production.

Disappointing results obtained on several farms, as well as in one departmental experiment, were traced to the use of limonite which was found to be of inferior grade. This product was not from the Whangarei deposit, and on changing over to the previously tested material from that source the trouble was quickly rectified. It is thus evident that field trials should precede the general use of limonite from any new source, and that producers should take care that only stone of the highest quality is ground for stock lick. Grittiness in even a good grade may make the limonite distasteful to sheep. The fineness of an excellent sample of Whangarei limonite recently analysed showed that 83 per cent. of material passed a 200-mesh sieve and that gritty particles were practically absent, everything passing a 60-mesh sieve.

Control of Ragwort.—In a few cases where inconclusive results attended the use of limonite it was considered that the animals were suffering from ragwort poisoning. The importance of controlling ragwort is, therefore, even greater in the bush-sick area than elsewhere, owing to the possibility of confusion of symptoms leading to wrong treatment and incorrect reports of the value of limonite for bush sickness.

The usefulness of sodium chlorate for ragwort destruction is somewhat diminished by the fire hazards attending its use. Trials are therefore being made with other substances to which this objection does not apply, in particular ammonium thiocyanate, which has given promising results in preliminary experiments.

Iodine Investigation.—The work has been actively prosecuted during the year. Several thousand thyroid glands, comprised in 760 samples, have been analysed for iodine-content. Lack of iodine is not shown in new-born calves except, possibly in cases of acute deficiency; the iodine is supplied from the body store of the mother. Analysis of samples of thyroids from sheep showed that the percentage of iodine increased with age, but no difference was observed either in size or iodine-content between male and female glands in 43 pairs of samples of lambs' thyroids.

The average weight of glands containing 0·03 per cent. iodine is 3·57 grm. Accepting this as a provisional standard, about 36 per cent. of the glands in Otago and Southland districts are enlarged above normal, while about 10 per cent. are grossly enlarged—*i.e.* weight over 6 grm.—the latter occurring at Mataura Island, Otama, Sterling, Milton, and Awamangu.

Experiments on the efficacy of iodised salt licks as a means of increasing the iodine-content of glands are at present being carried out in Southland under the supervision of the District Superintendent, glands from the various groups being forwarded as they become available.

Bitter Vegetable Marrow.—Two samples of vegetable marrow with an intensely bitter taste were received, one being grown in Wellington and the other imported from Australia. Both were immature and were regarded with apprehension by the purchasers, while vomiting had followed the eating of portions of one sample. The samples were too small for the identification of the bitter principle, which did not give any of the reactions for alkaloids. The family to which the vegetable marrow belongs (*Cucurbitaceae*) contains many poisonous species closely allied to the marrow, and under certain external conditions it is possible that even the cultivated species may produce poisonous fruits.

Cyprus

ANNUAL REPORT OF THE GOVERNMENT ANALYST FOR THE YEAR 1932

Dr. S. G. Willimott, the Government Analyst, reports that 2428 samples were examined during the year, 2399 of these being official, including 969 of food and drugs and 278 relating to criminal cases.

Food and Drugs.—For the purposes of the administration of the Food and Drugs Law, the Island is divided into seven districts. Of the 299 samples from the Nicosia district, 155 were adulterated, the remaining 40 adulterated samples being distributed over the other six districts.

Milk.—The legal standards at present in vogue in Cyprus are 3 per cent. of fat, and 8·5 per cent. of solids-not-fat. Milk for human consumption is derived from the cow, sheep or goat, and, with the possible exception of cows' milk, is usually mixed. With an average fat-content of 5·0 per cent. for sheep's milk, and of 4·5 per cent. for goats' milk, it is obvious that the prevailing standards are too low, and the experience of the last three years has shown that the fat-limit might well be raised to 3·25 per cent.

The experimental findings of Baker and Taubes (Analyst, 1932, **57**, 375) on the fluorescence of milk have been confirmed. The characteristic canary-yellow fluorescence of milk (cow, goat or sheep) cannot be attributed to the fat, as it is stated to be by Popp (Analyst, 1926, **51**, 540).

Coffee.—Twenty-seven of the 183 samples examined were adulterated with starch in proportions ranging from 7 to 65 per cent.

Olive Oil.—Of 35 samples, one was found to be adulterated with soya bean oil; apparently this practice is on the increase in Cyprus.

Mineral Water.—Every one of the twelve samples examined was condemned; they had been carelessly prepared from unsuitable water under obviously unsatisfactory conditions.

CRIMINAL EXHIBITS.—Many uses have been found for the ultra-violet lamp, especially in the examination of dangerous drugs and of cancelled postage stamps which have been re-used on receipt vouchers.

Counterfeit Coins.—The coins examined were of three types. Eight consisted of silver and copper, 11 of lead and tin, and six of tin. Two counterfeit English silver coins, which, from their excellence of manufacture, were evidently stamped, proved to be of almost pure tin.

QUININE POISONING.—Since the case recorded in 1931 (*Lancet,* Nov. 21, 1931, p. 1133) several other cases have been described. A forest guard attempted to commit suicide by taking 32 five-grain tablets of quinine sulphate, but the large dose caused prompt and repeated vomiting which ejected most of the alkaloid. After stomach lavage and treatment he recovered in 24 hours.

In another case a woman (aged 18) took 20 five-grain tablets of sugar-coated quinine hydrochloride in an attempt to procure abortion. The usual symptoms came on, and about 12 intact tablets were vomited. The patient remained unconscious for 6 hours, but afterwards made an uneventful recovery.

In November, 1932, a girl (3 years old) swallowed 8 five-grain tablets of sugar-coated quinine sulphate in mistake for sweets. After vomiting and purging, the child became cyanosed, but, after treatment, she made a slow recovery. It is questionable whether the danger of sugar-coated quinine tablets being taken by children does not far outweigh their advantages.

British Pharmaceutical Codex

CODEX REVISION COMMITTEE

REPORT OF DRESSINGS SUB-COMMITTEE*

THE Dressings Sub-Committee has summarised in a Report the Principal Standards for Surgical Dressings recommended by them and accepted, provisionally, for inclusion in the British Pharmaceutical Codex, 1934.

The substances proposed for inclusion in the next issue of the Codex include: (1) Basic materials such as jute, silk and wool, for which the sub-committee have prepared monographs giving descriptions of the characters of these substances, (2) dressings such as phenol gauze, mercuric chloride gauze, euflavine gauze, and phenol tow, for which the sub-committee have not recommended the inclusion of a quantitative standard for the proportion of medicament present, and (3) the more important dressings for which revised requirements have been prepared. It is with the last group of substances that this summary deals.

The summary has been prepared in the hope that it will provide information useful to manufacturers and others. The Editor of the ***British Pharmaceutical Codex*** (17, Bloomsbury Square, W.C.1) will welcome comments on the standards proposed or suggestions for the improvement of the tests and will give careful consideration to all communications relating to them.

* Published by the Direction of the Council of the Pharmaceutical Society of Great Britain. The Pharmaceutical Press, 23, Bloomsbury Square, W.C. 1. Price 1/6.

Pharmacy and Poisons Act, 1933

POISONS BOARD

THE following members of the Poisons Board have been appointed under Section 16 of the Pharmacy and Poisons Act, 1933 (*cf.* ANALYST, 1933, **58**, 548):

	Appointing authority
Sir Gerald Bellhouse, C.B.E. (Chairman)	Secretary of State for the Home Department
Sir Walter Greaves-Lord, K.C., M.P.	Do. do.
Sir William George Lobjoit, O.B.E., J.P.	Do. do.
W. H. Whitelegge, Esq.	Do. do.
J. M. Johnstone, Esq., M.B., Ch.B., F.R.C.S.(Ed.)	Secretary of State for Scotland
J. N. Beckett, Esq.	Ministry of Health
F. McCleary, Esq., M.D.	Do.
H. E. Dale, Esq., C.B.	Do.
Sir Robert Robertson, K.B.E., D.Sc., LL.D., F.R.S. (or Deputy)	*Ex officio* as Government Chemist
J. H. Franklin, Esq.	Pharmaceutical Society of Great Britain
H N. Linstead, Esq.	Do. do.
G. A. Mallinson, Esq.	Do. do.
E. T. Nethercoat, Esq.	Do. do.
P. Sparks, Esq., C.B.E., J.P.	Do. do.
Sir William Willcox, K.C.I.E., C.B., C.M.G., M.D., B.Sc.	Royal College of Physicians of London
R. Stockman, Esq., M.D., LL.D., F.R.C.P.	Royal College of Physicians of Edinburgh
S. A. Smith, Esq., M.D., M.R.C.P., D.P.H.	General Medical Council
Gerald Roche Lynch, Esq., O.B.E., M.B., F.I.C.	Council of the Institute of Chemistry of Great Britain and Ireland
J. W. Bone, Esq., M.D.	British Medical Association

The Board has appointed Mr. M. D. Perrins of the Home Office as Secretary, to whom any communications to the Board should be addressed.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs Analysis

Determination of Nitrogen in Yeast and Brewing Materials. W. A. Davis, J. G. Maltby, and F. E. Salt. (*J. Inst. Brewing*, 1933, **39**, 577–581.)—The authors confirm the conclusion of J. S. Ford *et al.* (ANALYST, 1933, **58**, 618), that almost identical results are obtained by the Kjeldahl–Gunning–Arnold method and by the Christensen and Fulmer modification for brewers' and bakers' yeasts sampled at different stages of manufacture or after undergoing different treatments, and for pure nucleic acid; the difference was about 0·5 per cent., and the latter method usually gave the higher results. The suggested explanation of the contradictory results of previous workers is the difficulty in determining the exact amount of nitrogen in the hydrogen peroxide used, as stabilisers of different types are used by different makers. Thus (*e.g.*) Merck's "perhydrol" contains uric or barbituric acid, and other manufacturers use urea, lecithin, casein, gelatin, etc., or even non-nitrogenous stabilisers, such as salicylic acid, resorcinol, phosphates, guaiacol, etc. In order to obtain an accurate "blank" 0·5 grm. (in some cases 1 grm.) of sugar of known nitrogen-content should be added to ensure the complete conversion of the nitrogen into ammonia during the digestion with sulphuric acid; when this is omitted only one-tenth of the blank is obtained. It is also pointed out that the Dumas method may give high results owing to the presence of unburnt methane in the nitrogen measured (*cf.* Dunstan and Carr, *Proc. Chem. Soc.*, 1896, 48), and that the method of Haas (*J. Chem. Soc.*, 1906, 570), in which copper oxide is replaced by lead chromate, eliminates this error. Similarly, lead chromate may be used with advantage in the ordinary Liebig combustion process for carbon and hydrogen; it shortens the process, avoids low results due to unburned methane, and enables the method to be used when halogens and sulphur are present. Ter Meulen's hydrogenation method (ANALYST, 1932, **57**, 524) gave excellent results for glycine if care was taken to remove all nitrogenous matter from the nickel formate, but with yeast the results were always about 5 per cent. lower than those obtained by the Kjeldahl–Gunning–Arnold method. The evolution of ammonia was slow, being incomplete after 2 hours, but this might have been due to an inactive catalyst. J. G.

Detection of Ketoses by a Microscopic Method. M. Wagenaar. (*Pharm. Weekblad*, 1933, **70**, 1029–1034.)—One mgrm. of the sugar is suspended in a drop of a 2 per cent. solution of α-naphthol in glycerin (sp.gr. 1·26), which is then brought into contact with a drop of hydrochloric acid of equal size. With glucose, lactose, arabinose or maltose the drop remains colourless; with rhamnose or galactose a slight colour is developed; whilst fructose, sucrose or raffinose produces a deep blue or blue-violet colour. The sensitiveness is normally 1 per cent., but 0·1 per cent. of cane sugar in milk sugar is detectable. The reaction distinguishes ketose from aldose sugars (*cf.* the hydroxymethyl furfuraldehyde test, and L. Ekkert, *Z. anal. Chem.*, 1930, **80**, 229), but is not specific for individual sugars. J. G.

Californian Honeys. W. Bartels and A. Fauth. (*Z. Unters. Lebensm.*, 1933, **66**, 396–407.)—Many North American, especially Californian, honeys show abnormally low diastatic activities, although no evidence is available that such honeys have been heated or that the bees have been sugar-fed. The results now given for many of these honeys fail to reveal any relationship of either the floral origin or the number of pollen grains of the honey to the diastase-content. It is suggested that the high temperatures occurring in many districts of California may be answerable for the low enzymic content of the honey, this view being supported in some cases by examination of the pollen present. T. H. P.

Detection of Sorbitol in Presence of Dulcin and Saccharin. G. Reif. (*Z. Unters. Lebensm.*, 1933, **66**, 408–412.)—Adulteration of wine with cider or perry may be demonstrated by showing the presence of sorbitol (*cf.* Werder, ANALYST, 1929, **54**, 476), which may be detected (1) by the formation of its hexacetyl compound, or (2) by the colour reaction of its benzylidene derivative with acetone in presence of sulphuric acid; in this case it is the benzaldehyde liberated which gives the coloured compound with the acetone. Possible disturbance of these reactions by the presence of "dulcin" (*p*-phenetole carbamide) or "saccharin" (*o*-benzoic sulphimide) is considered by the author. It is found that benzaldehyde and dilute sulphuric acid (1:1) act on dulcin, giving benzylidenedulcin, with formation of a red colour; that dulcin forms a crystalline acetyl compound, and that treatment of benzylidenedulcin with aqueous sulphuric acid and acetone results in the liberation of benzaldehyde and the appearance of a yellowish-red colour. Unlike sorbitol, dulcin is, however, completely adsorbed by the carbon used in Werder's test, and hence does not interfere with the tests. Saccharin behaves differently, as it yields no benzylidene derivative; moreover, it produces no coloration with acetone and sulphuric acid, it is completely adsorbed by carbon, and, if the acetylation test is used, is entirely removed during the procedure followed. The effect of mannitol on the tests is also considered, and the following methods of carrying out the test are recommended:

From 100 to 130 ml. of the wine are heated with carbon and filtered by suction through Seitz filtering material. Distillation and treatment with sulphuric acid (1:1) and benzaldehyde are effected as usual, and the product is left for 24 hours in a cold room (best 7° C.). The subsequent procedure is varied according to the amount of the benzylidene sorbitol formed. With a relatively large amount, the residue is washed from the flask with 100 ml. of cooled water into a beaker and left for 30 minutes. It is then filtered by suction on to a fritted glass crucible (grain size 1 G2), and washed, first with about 100 ml. of water (lumps being broken up with a glass rod), then with two portions (5 to 10 ml.) of an ice-cold mixture of 3 parts of absolute alcohol and 7 parts of petroleum spirit, and, finally, twice with at least 10-ml. quantities of petroleum spirit; before each addition of washing liquid, the suction is interrupted so that the precipitate may be thoroughly mixed with the added liquid. The precipitate is then dried in the crucible or on a watch-glass for 30 to 60 minutes at 75° to 80° C. To a small portion (0·01 to 0·03 grm.) of the dry precipitate—which should be practically colourless—in a test-tube, 0·9 ml. of water and 0·3 ml. of pure acetone are added, and the whole is mixed by swirling the tube; 0·52 ml. of concentrated sulphuric acid (sp.gr. 1·84) is then pipetted rapidly on to the middle of the liquid surface, and the swirling is repeated. If benzylidenesorbitol is present, the crystals dissolve, and the acid liquid assumes, either at once or after a few minutes, an orange-red colour, which reaches its full strength after about 15 minutes. If only benzylidenemannitol is present, the crystals dissolve, but the liquid either remains colourless or turns yellow. If less than 0·01 grm. of precipitate forms, it is best collected on a small filter-paper in a Gooch crucible, washed with 20 ml. of water, two 3-ml. quantities of the alcohol-petroleum spirit mixture, and two 10-ml. quantities of petroleum spirit, no interruption of the suction or stirring being necessary. After being dried for 30 minutes at about 75° C., the paper, folded with the precipitate inside, is transferred to a test-tube and 0·45 ml. of water and 0·15 ml. of acetone are added. The filter is pressed into the liquid with a rod, 0·26 ml. of sulphuric acid is added, and the tube is swirled. The orange-red colour may take an hour to develop. This procedure shows clearly the presence of 3 per cent. of cider in wine and gives a faint pink colour even with 2 per cent. T. H. P.

Detection and Determination of Diacetyl in Butter. W. L. Davies. (*Food Manufacture*, **1933, 8,** 346–348.)—To detect traces of diacetyl in butter, the diketone may be condensed with hydroxylamine to form dimethylglyoxime, which yields a red nickel compound. Also, the Voges-Proskauer reaction may be used; *viz.* in strong alkaline solution diacetyl gives a deep red colour with various compounds containing a guanidine nucleus, such as peptone solution or creatine. As little as 1/100 mgrm. of diacetyl may thus be detected, but the depth of colour is not proportional to the amount present. To determine the diacetyl, the nickel glyoxime method is used. From 0·5 to 1 kilo. of butter is distilled in the presence of 500 ml. of a mixture of 0·1 *N* sulphuric acid and 1 per cent. acetic acid, and a drop of oleic acid is added to oxidise any carbinol to diacetyl. The mixture is heated for 20 minutes in an all-glass apparatus beneath a reflux condenser, and 40 ml. of distillate are then collected and kept at 90° C. for 1 hour after being mixed with 10 ml. of a buffered nickel reagent (1 part of 20 per cent. hydroxylamine hydrochloride, 1 part of 10 per cent. nickel sulphate solution, 2 parts of 20 per cent. sodium acetate solution). After the liquid has been cooled and neutralised to a p_H of 7·2 the nickel compound is left to settle for 24 hours; the liquid is then filtered through a tared sintered Jena crucible (IG_3), the precipitate is dried at 110° C. and weighed, and the weight is multiplied by 0·596 to obtain the weight of diacetyl. Repeated determinations of known amounts of diacetyl gave results with 97 to 103 per cent. of theory. If the diacetyl is to be estimated from the intensity of the red colour on Gooch filter discs (*cf.* ANALYST, 1932, **57,** 389), 40 to 100 grms. of butter and 100 ml. of water are directly distilled, and no neutralisation is necessary. D. G. H.

Determination of the Insoluble Bromide Values of Oils [in Cans of preserved Fish]. R. Marcille. (*Ann. Falsif.*, 1933, **26,** 393–398.)—The amount of fish oil in the covering oil of preserved fish is calculated from the proportion of insoluble bromides yielded by the oil in the can. One grm. of the oil is weighed into a tared centrifuge tube, 30 c.c. of ether are added, and the tube is corked and placed in a little iron wire support in a crystallising apparatus filled with ice and water. After 10 minutes, bromine is gradually added, 0·20 to 0·25 c.c. at a time, with mixing, after each addition, at intervals of 10 to 15 seconds, until a distinct red colour is obtained, about 0·5 to 1·5 c.c. of bromine being required. The tube is left in the ice-water for at least 3 hours; any clear liquid is then poured off and the tube is centrifuged for a few minutes, after which decantation is easy. Three to 4 c.c. of ether (previously chilled in ice-water) are poured down the side of the tube, the precipitate is detached from the bottom with a small rod of hardwood or bone, and the contents are mixed with a circular movement. The tubes are again centrifuged, the precipitate is washed with a further 10 to 11 c.c. of chilled ether, and, after a final centrifuging, the solvent is driven off, the tube warmed to 90 to 100° C., and subsequently weighed. The insoluble bromide value is taken as the weight of the derivatives given by 100 grms. of oil. Five per cent. of fish oil in either olive or arachis oil gave a value of 60; 10 per cent. a value of 63; 20 per cent. a value of 68; 40 per cent., 77; 60 per cent., 80·5; and 100 per cent., a value of 85. It was found that the weight of bromine derivative was not proportional to the content of the oil in the mixture. This applied to both linseed oil and fish oil, and no difference in this respect was observed whether the diluting oil was olive, or arachis. Linseed oil, either in China wood oil or in jequirity oil, gave the following values:

Linseed oil, per cent... ..	5	10	20	40	70	100
Insoluble bromide, per cent...	28	29	33·5	36	44·4	47

Commercially, pure linseed oils should always give a value exceeding 45. D. G. H.

Analysis of Oils in Cans containing preserved Fish. R. Marcille. (*Ann. Falsif.*, 1933, **26**, 398–403.)—To make use of the insoluble bromide values of the fish oils to determine the proportion of the oil in the vegetable covering oil in cans of preserved fish, it is necessary to know the constants of the pure fish oils, and these oils are not easy to procure. Authenticated samples of certain oils gave the following figures:—Two sardine oils (1930 and 1931) obtained from fish prepared for cooking and canning; $n_{\text{D}}^{20^\circ}$, 1·4826, 1·4805; insoluble bromide value, 85, 71; iodine value, 185, 175. Oil recovered from fish waste, by boiling with water, $n_{\text{D}}^{20^\circ}$, 1·4806, insoluble bromide value 71; iodine value 177. Sardine oil from Sablesdes Olonne (1932); fish and waste oil (August, 1932); sardine oil from Quiberon (October, 1932); and tunny fish oil from Tunis, $n_{\text{D}}^{20^\circ}$ 1·4805, 1·4826, 1·4826, 1·4813; insoluble bromide value, 69, 84·4, 85, and 80, respectively. Probably the oils with the lower values are from immature fish. To determine the proportion of fish oil in the covering oil, the following table is used.

Percentage of fish oils	Insoluble bromide values		
	Small sardines	Ordinary sardines	Tunny fish
5	50	60	60
10	51	63	60
20	54	68	65
40	60·5	77	61
60	63	80·5	72·5
100	69	85	80

The refractive indices and iodine values are used as criteria of the purity of the vegetable oil used. The method was checked by applying it to a box of sardines in oil, accompanied by a sample of the olive oil used for preservation. The covering oils (originally olive oil) in boxes of sardines vary greatly in composition, some containing about 25 per cent. of fish oil and others as little as 5 per cent. Preserved tunny fish usually has but little fish oil in the covering oil. D. G. H.

Determination of Fish Fat in Sardines in Oil. G. Lunde and E. Mathiesen. (*Z. Unters. Lebensm.*, 1933, **66**, 435–444.)—Unsuccessful attempts have been made to determine fish oil when mixed with olive oil by means of the polybromide value (*cf.* Hehner and Mitchell, ANALYST, 1898, **23**, 310) and the iodine value. For quantitative purposes, Bull and Saether's method (*Chem.-Ztg.*, 1910, **34**, 733) is found useless. Approximately correct results are, however, obtainable by making use of the refractive index, which varies only from 1·4743 to 1·4764 (mean for 18 samples 1·4755) for the oil of *Clupea sprattus* at 25° C., and from 1·4672 to 1·4673 for Spanish olive oil, and from 1·4675 to 1·4677 for

French olive oil (mean for olive oil 1·4673). With mixtures of the olive and fish oils the refractive index is almost exactly additive.

After the gross weight of the tin has been determined, the oil is centrifuged, if necessary, to remove water, and is then filtered through a dry filter. The sardines are transferred to a porcelain basin, and the tin is rinsed out with ether, which is added to the fish in the basin. The ethereal solution is passed through the original filter into a weighed flask. The sardines are then intimately mixed with anhydrous sodium sulphate and the mixture extracted with ether in a Soxhlet apparatus. The ethereal extracts are evaporated *in vacuo* at 40° C., the dried oil is added to the filtered oil, and the total oil is weighed. The refractive index gives the proportions of sardine and olive oils present in the mixture, and the percentage of this in the contents of the tin can be calculated. If the fish have been subjected to preliminary drying by smoking, the oil-content is increased in proportion to the loss of water. A curve is given which shows the relationship between the percentages of oil in the fresh and smoked fish, so that results obtained with smoked fish may be converted into those for the fresh fish. T. H. P.

The Taffel and Revis Method for Estimating the Rancidity of Oils and Fats. J. K. Giles. (*J. Soc. Chem. Ind.*, 1933, **52**, 816–817.)—Practical experience of the Taffel and Revis 1(*b*) method (ANALYST, 1931, **56**, 323) for estimating the rancidity of fats that have become rancid at moderate temperatures, *i.e.* the method as applied to solid fats, shows that in dealing with fats of very slight rancidity, the variability of the blank limits the application of the test, and the following modification of the test has therefore been adopted: About 11 ml. of the melted fat are poured into a 10-ml. measuring cylinder (counterpoised to 0·05 grm.) and kept warm. Forty ml. of glacial acetic acid are placed in a 2-oz. bottle, which is clamped up to the neck in water at 95° to 100° C., and a stream of carbon dioxide is passed through by means of a tube drawn out to a fairly fine capillary. After 2 minutes, 2 ml. of 50 per cent. potassium iodide solution are run in without stopping the carbon dioxide; not more than a very light yellow tint should appear. After another minute the liquid fat is added (the cylinder being re-weighed), and the stream of carbon dioxide is continued for 4 minutes. The contents of the bottle are poured into 150 ml. of water in an 8-oz. wide-mouthed stoppered bottle, the tube and bottle being rinsed. Starch solution is added, and the liquid is titrated with 0·5 *N* thiosulphate solution. The final colour is yellow or gray, and the end-point is reached when 2 drops of thiosulphate solution fail to give a distinct brightening of the colour. A blank test is made. Volatilisation of iodine was found to be within the error of experiment. D. G. H.

Täufel and Thaler's Reaction for Ketone Rancidity. J. Pritzker and R. Jungkunz. (*Chem.-Ztg.*, 1933, **57**, 895–896.)—Fortner and Rotsch's observation (*ibid.*, 1933, **57**, 714) that undoubtedly fresh table butter sometimes gives Täufel and Thaler's reaction for ketone rancidity (ANALYST, 1932, **57**, 466) is confirmed, and it is found that the reaction is shown by acetylmethylcarbinol, but not by diacetyl. The presence of acetylmethylcarbinol in the distillate to be tested may be avoided by distillation with ferric chloride, which does not affect methyl ketones. The reaction is applicable to highly acid fats, since the volatile fatty acids of butter-fat do not react. The following modification of Täufel and Thaler's procedure is recommended:

The fat is distilled in Pritzker and Jungkunz's apparatus for water determination (*Chem.-Ztg.*, 1929, 603), which is provided with a 200-ml. Erlenmeyer flask and a pendant condenser. The cock of the apparatus is adjusted so that the distillate collects in the upper part and no reflux to the flask occurs. No cork or rubber is used in the connections. Thirty grms. of the butter, 120 ml. of water, 30 ml. of ferric chloride solution (German Pharmacopoeia), and a few small pieces of glass tubing or porcelain are placed in the flask and 30 to 40 ml. are distilled over. The distillate is collected in a tube (about 50 ml.) with ground stopper, and 0·4 ml. of the salicylaldehyde reagent is added. The whole is shaken vigorously for 3 minutes and centrifuged, the water being then poured off carefully to leave about 4 ml. After further shaking for a short time, the emulsion is treated with 2 ml. of concentrated sulphuric acid, which is poured into the liquid and not down the wall of the tube. After thorough mixing, the aldehyde layer separating becomes yellow in absence of ketones, but shows a deepening pink or red colour if even traces of ketones are present. A faint coloration may be intensified by immersing the tube for 15 minutes in a boiling water-bath. T. H. P.

Production of Pseudomorphine from Morphine. C. C. Fulton. (*Amer. J. Pharm.*, 1933, **105**, 503–510.)—Although pseudomorphine may be produced from morphine by simple or catalytic oxidations, the oxidations are difficult to control. By dissolving morphine in dilute alkali, or a salt of morphine in water, and adding sodium hydroxide to slight excess with subsequent addition of potassium ferricyanide until no more is reduced, a yield of about 90 per cent. of pseudomorphine may be obtained. A similar yield may be obtained by heating morphine with a salt of mercury, *e.g.* mercurous chloride. A yield of about 75 per cent. may be obtained by catalytic oxidation with persulphate as oxidising agent, copper as catalyst, and pyridine as the substance with which copper forms an effective complex. The formation of pseudomorphine may be used as a characteristic and fairly simple test for morphine by making use of the strong green colour formed with Marquis' reagent. To 0·5 ml. of morphine solution is added 1 drop of 10 per cent. sodium carbonate solution (in addition to that required for neutralisation), and then, drop by drop, 1 per cent. potassium ferricyanide solution until the solution is distinctly yellow. From 1 to 2 ml. of concentrated sulphuric acid are introduced beneath the liquid, 1 drop of 37 to 40 per cent. formaldehyde solution is added, and the whole is mixed while being cooled with running water. The green colour produced will detect 1 part of morphine in 3000. If formed gradually, pseudomorphine will be precipitated as crystals of characteristic structure. D. G. H.

Properties of Pseudomorphine. C. C. Fulton. (*Amer. J. Pharm.*, 1933, **105**, 511–513.)—Pseudomorphine, the first oxidation product of morphine, is formed from 2 mols. of morphine by the removal of 2 hydrogen atoms, and oxidation may easily proceed further. It is a natural constituent of opium, to the extent of 0·02 to 0·04 per cent., but is physiologically inert. It contains 4 hydroxyl groups, and is a phenol of similar kind to morphine. Pseudomorphine is a weak base, insoluble in water, and, when precipitated slowly, or from hot acid solution by ammonia, forms small square leaflets, silky needles, or occasionally diamond or 4-pointed star-shaped crystals. If formed rapidly it is amorphous. When the precipitate is washed with distilled water or alcohol it gradually forms a colloidal solution and passes through the filter, but this may be prevented by addition of an electrolyte. Although fairly soluble in most acids, the salts with mineral acids are less so than those of most alkaloids, the sulphate being insoluble. It is readily soluble in acetic acid, is precipitated by ammonia, but is soluble in excess of alkali. It is insoluble in ordinary solvents, and resembles other weak insoluble alkaloids of opium in its precipitation reactions with alkaloidal reagents. Its colour reactions are numerous. Although pseudomorphine may be formed in many oxidations of morphine, it is not a necessary stage. The formation of pseudomorphine from morphine can be made almost quantitative, and it may be used as a test for aldehydes. D. G. H.

Biochemical

Colorimetric Determination of Tryptophan in the Haemolymph of the Silkworm. L. Mamoli. (*Giorn. Chim. Ind. Appl.*, 1933, **15**, 437–438.)—The tryptophan was determined colorimetrically by Fürth and Nobel's modification (ANALYST, 1921, **46**, 293) of Voisenet's reaction: 1 ml. of the haemolymph, 1 drop of 2·5 per cent. formaldehyde solution and sufficient concentrated hydrochloric acid to make the volume up to 15 ml. were shaken in a ground-stoppered graduated 25-ml. cylinder; after addition of 10 drops of 0·05 per cent. sodium nitrite solution, the volume was made up to 20 ml. with concentrated hydrochloric acid. The violet colour, which reached its maximum intensity after 5 or 10 minutes, was compared in a Duboscq colorimeter with that given similarly by 0·1 per cent. tryptophan solution (containing 2 per cent. of sodium fluoride to prevent decomposition). Six samples of the haemolymph showed from 0·150 to 0·163 (mean 0·152) per cent. of tryptophan. It is suggested that, in the silkworm and possibly in other insects also, digestion of proteins proceeds as far as the liberation of free amino-acids. T. H. P.

Seasonal Variation in Butter-fat. I. Seasonal Variations in Carotene, Vitamin *A* and the Antimony Trichloride Reaction. R. G. Booth, S. K. Kon, W. J. Dann, and T. Moore. (*Biochem. J.*, 1933, **27**, 1189–1196.)—During an investigation of the seasonal variations in the vitamin-content of typical English milk several unexpected difficulties were encountered in accepted routine biological tests, and it was necessary to seek new explanations of the observed facts. This was the case when it was attempted to apply the well-known colorimetric and spectroscopic methods to the determination of carotene and vitamin *A* in butter-fats, and the report is concerned with attempts to overcome this difficulty. The seasonal variation in the carotene and vitamin *A* contents of typical English butter from shorthorn cows was followed by colorimetric methods. Determinations of the intensity of yellow colour were carried out on the untreated butter-fats.

Antimony trichloride blue values were determined both on the untreated fats and the corresponding non-saponifiable residues. Data obtained on yellow colour and blue value, as determined on the non-saponifiable residue, agreed well with the established variation of the carotene and vitamin *A* contents of the butter, corresponding with the quantity of grass or of green fodder available in the diet of the cow. Blue values determined on the untreated butter-fat were found to be valueless as a guide to vitamin *A* content, being 5 to 10 times lower than values determined on the non-saponifiable matter. Although blue values determined on the untreated fats showed no consistent quantitative variation, qualitative differences in the behaviour of the blue colours produced by "winter" and "summer" butter-fats were observed. These differences were connected with an inhibitory substance or substances, present in much larger concentration in "summer" than in "winter" butter-fats, whose presence could be detected from its inhibitory power on the blue colour given by vitamin *A* when added from an external source. It is pointed out that in the practical assay of the total vitamin *A* activity of butter-fats by colorimetric means both the vitamin *A* and carotene contents should be taken into account. A provisional formula for calculation of the total vitamin *A* activity is suggested. Assuming from recent work that 2 yellow units of carotene are roughly equivalent to 5 blue units of vitamin *A*, and accepting the international standard of vitamin *A* activity as referring to 1γ of pure carotene, the total activity of a given sample of butter-fat is calculated as follows:

$$\frac{\text{Y.U. per grm.}}{2} + \frac{\text{B.U. (non-sap)}}{5} = \text{international units per grm.}$$

The total vitamin *A* activity of summer butter-fat from shorthorn cows appears to be some 3 times greater than that of winter butter-fat. The fraction of the total activity due to carotene is also greater in summer butter-fat. The authors hope to deal with spectroscopic variations in winter and summer butter-fats in a subsequent communication. P. H. P.

Absorption Spectra of the Mixed Fatty Acids from Cod-liver Oil. W. J. Dann and T. Moore. (*Biochem. J.*, 1933, **27**, 1166–1169.)—Previous workers have shown that there is a surprising difference between the absorption spectrum of cod-liver oil itself and that of the mixed fatty acids derived from it. Cod-liver oil itself was found by Morton and Heilbron (ANALYST, 1928, **53**, 664) to have relatively low absorption ($E^{1\%}_{1\,\text{cm.}}$ =1·2 for a good oil) in the ultra-violet, characterised by the broad unbroken band of vitamin *A* at $328m\mu$. On the other hand, Gillam, Heilbron, Hilditch, and Morton (ANALYST, 1931, **56**, 471) found that the mixed acids and unsaponifiable matter, obtained by acidification and ether extraction of the hydrolysate, had so intense an absorption ($E^{1\%}_{1\,\text{cm.}}$ at $270m\mu = 250$, at $230m\mu = 190$) as to obscure the presence of the admixed vitamin *A*. The absorption, moreover, was characterised by fine structure, showing not only a band at $230m\mu$, but also 9 other narrow absorption bands. The change was irreversible, and it was suggested that under the conditions of hydrolysis a substance (or substances) accompanying vitamin *A* gives rise to acid decomposition products which display intense selective absorption. The authors have now discovered that the duration of the saponification process exerts such a profound influence upon the absorption spectrum as to make data obtained under uncontrolled conditions of saponification almost meaningless. They found that the mixed fatty acids prepared from a typical cod-liver oil by a brief saponification, removal of the non-saponifiable matter by ether, acidification, and ether extraction, showed only relatively low absorption in the ultra-violet region without fine structure ($E^{1\%}_{1\,\text{cm.}}$ 230$m\mu$ = 6·5). If, however, the time taken for the saponification was prolonged, or if the separated acids were boiled with a further supply of alcoholic potassium hydroxide, the absorption became much more intense ($E^{1\%}_{1\,\text{cm.}}$ 230$m\mu$ after 12 hours = 72), and definite signs of fine structure became evident. Whether this phenomenon can be regarded as a complete explanation of the observations of Gillam and his colleagues cannot be decided with certainty, since these workers have given no details of their technique in saponification.

P. H. P.

Regeneration of the Reducing Properties of Oxidised Lemon Juice. S. W. Johnson. (*Biochem. J.*, 1933, **27**, 1287–1289.)—The observation of Tillmans, Hirsch and Dick (*Z. Unters. Lebensm.*, 1932, **63**, 267), that lemon juice oxidised with indophenol, iodine or hydrogen peroxide can regain its reducing capacity when treated with hydrogen sulphide immediately after oxidation, is confirmed. Various difficulties were encountered in repeating the work. It was found necessary to use juices in which no traces of iron were present, as this vitiated the results. The major difficulty was the complete removal of the hydrogen sulphide. However, it was found that after passing nitrogen for about 3 hours, except in the case of oxidations with hydrogen peroxide, the persistent residuum of hydrogen sulphide was insufficient to affect appreciably the titrations. The juices were considered to be free from hydrogen sulphide when the issuing gas failed to decolorise a solution containing 1 ml. of $N/1000$ indophenol when bubbled through it for half-an-hour. The ratio between the capacity of lemon juice for reducing iodine in acid solution and indophenol in neutral solution was almost invariably constant, and the amounts of these reagents reduced were roughly equivalent. Good agreement between indophenol and iodine titrations of the oxidised and untreated juices, and the absence of hydrogen sulphide in the above test, were therefore regarded as criteria that regeneration had been effected. Experiments in which indophenols were used as oxidising agents gave rather low results after regeneration; in these experiments also no iodine titrations could be undertaken, as the indicator interfered. The experiments with iodine as oxidising agent gave the most satisfactory results, both with decitrated lemon juice and the raw juice. Since hydrogen peroxide functions most satisfactorily in an acid medium, oxidations with this reagent were carried out on the raw juice. Some typical experiments are described, and the results obtained are given. P. H. P.

Vitamin *C* in *Citrus* Juices. A. H. Bennett and D. J. Tarbert. (*Biochem. J.*, 1933, **27**, 1294–1301.)—The recent work of Svirbely and Szent-Györgyi (*Biochem. J.*, 1933, **27**, 279) has brought almost conclusive proof of the identity of vitamin *C* and the ascorbic acid which can be prepared from orange juice, paprika, or suprarenal glands, and several workers have shown that there is a close connection between the amount of ascorbic acid as determined by titration with Tillmans' reagent, dichlorophenolindophenol, and the antiscorbutic value of the material examined. This method of titration has been applied to the examination of a number of samples of lemon and orange juices, both freshly prepared and preserved in various conditions, with the object of ascertaining the degree of natural variation in the content of ascorbic acid and the conditions which determine its preservation or disappearance in storage. It has been found that: (*a*) The reducing power of fresh lemon juice is subject to considerable variation; the lowest samples examined had only 60 per cent. of the reducing power of the highest. (*b*) The reducing power of orange juice is more constant and rather higher than that of lemon juice. (*c*) The reducing power of both juices does not diminish much in storage in the absence of preservatives, but the use of any preservative which is efficient in preventing fermentation is followed by the gradual diminution of the reducing power, which totally disappears in, at most, a few weeks. (*d*) The same result is brought about by strong acidification, pasteurisation, or boiling. It is concluded that in untreated juice the reducing factor is protected from atmospheric oxidation by the action of an enzyme, and that when this action is inhibited by any of the usual means the reducing power is rapidly lost. P. H. P.

Vitamin *D* Activity of Butter. I. Chemical Differentiation of the Anti-rachitic Factor of Autumn and Winter Butter from Irradiated Ergosterol and the Vitamin *D* of Cod-liver Oil. S. K. Kon and R. G. Booth. (*Biochem. J.*, 1933, **27**, 1302–1309.)—In a series of experiments to determine the vitamin *D* in butter in winter, summer and autumn by curative and protective experiments on rats, the butter-fat was administered to the experimental animals by pipette separately from the diet, and it was found almost impossible to give to the rats more than 1·5 grms. (or almost 2 ml.) of butter daily. When planning curative experiments it was decided to concentrate the anti-rachitic factor of butter by saponification and to feed to rats the non-saponifiable residue of larger quantities of butter, 3 and 6 grms. daily. In order to test the feasibility of such a method, the anti-rachitic effects of graded amounts of autumn butter have been compared in protective experiments with those of equivalent amounts of the non-saponifiable residue from this butter. It is shown that autumn and winter butters, either saponified in the usual way by boiling for 1 hour on the water-bath with alcoholic potassium hydroxide, or by heating with alkali for 2 minutes only, lose a large part (over 80 per cent.) of their anti-rachitic potency, as determined by prophylactic experiments on rats. Under exactly similar conditions irradiated ergosterol (the International Standard of vitamin *D*) or cod-liver oil can be subjected to saponification either alone or mixed with butter without loss of potency. The fact that the stability to saponification of the anti-rachitic factor of cod-liver oil and of irradiated ergosterol is not adversely influenced by the presence of butter speaks against the existence in butter of a specific destructive factor, and in favour of a true chemical difference between the anti-rachitic factor of butter and those of cod-liver oil and irradiated ergosterol. P. H. P.

Bacteriological

Use of some Micro-organisms in Sugar Analysis. V. J. Harding and T. F. Nicholson. (*Biochem. J.*, 1933, **27**, 1082–1094.)—A number of micro-organisms have been examined as possible analytical reagents for sugars. A close relationship between sugar-removal power and fermentation has been shown. Four of the organisms examined appear useful as biological reagents for sugars. A strain of *Proteus vulgaris* has been developed as an analytical reagent for glucose. *Proteus* is without removal action on fructose, mannose, maltose, lactose, sucrose, arabinose and xylose, but is variable towards galactose. *Proteus* can be applied to Folin-Wu blood-filtrates and to urines after treatment with sulphuric acid and Lloyd's reagent, and after treatment with mercuric sulphate and barium carbonate. Details of the analysis of mixtures of glucose, fructose, and sucrose are given. *Monilia tropicalis* is extremely active in removal of maltose. A method for the determination of maltose is given, which depends on the use of *Saccharomyces marxianus*, followed by *Monilia tropicalis*. Baker's and brewer's yeasts show variations in their removal power towards maltose, depending on the freshness of the organism. A method with the use of "aged" and "fresh" baker's yeast for the separation of glucose and maltose is suggested. *Monilia krusei* is a useful sugar reagent, as it removes only glucose, fructose and mannose. From these results and those of Harding, Nicholson and Grant (*J. Biol. Chem.*, **1932–33, 99, 625**), a system of carbohydrate analysis has been constructed and is outlined. A mixture of glucose, fructose or mannose, galactose, sucrose, maltose, and lactose can be analysed by the use of *Proteus vulgaris, M. krusei, S. marxianus,* and *M. tropicalis,* combined with acid hydrolysis at appropriate stages; the following steps are necessary: A. Determine *glucose, fructose, mannose* by *M. krusei*. B. Determine *galactose* on the residual fluid from A by *S. marxianus*. C. (In absence of galactose) determine *glucose* by *Proteus vulgaris*. A–C = *fructose-mannose*. D. (In presence of galactose) determine *fructose-mannose* on residual fluid from C by *M. krusei*. A–D = *glucose*. E. Determine *sucrose* on residual fluid from A or D by hydrolysis, followed by use of *Proteus vulgaris* and *M. krusei*. (In presence of galactose or maltose calculate the sucrose from the fructose value.) F. Determine *maltose* by *S. marxianus* followed by *M. tropicalis*. G. Determine *lactose* on fluid from F by hydrolysis. Calculate the lactose from the galactose value, assuming 72 per cent. hydrolysis. The determinations A, C, F are made on the original mixture. The details of analysis of the six sugars each present at a concentration of 10 mgrms./100 ml. have been given in a previous paper by Harding, Nicholson, Grant, Hern and Downs (*Trans. Roy. Soc. Can.*, 1932, **26**, (5), 33). The following table shows the percentage recovery of the sugars from mixtures analysed by the biological reagents:

	I	II
Glucose	97·6	95·4
Fructose	101·7	101·1
Galactose	96·7	100·8
Sucrose	103·0	103·0
Maltose	109·6	105·1
Lactose	98·8	106·2

Some precautions in the use of organisms as analytical reagents for sugars are suggested.

P. H. P.

Bacterial Activity in the Hot Springs at Aachen and Aachen-Burtscheid. A. Brussoff, F. Reinartz and A. Schloemer. (*Z. Unters. Lebensm.*, 1933, **66**, 446–453.)—Stony and sandy lime deposits from these springs proved to be bacteriogenic in origin. Lime- and iron-storing bacteria, and also bacteria which deposit silicic acid, take part in their formation. T. H. P.

Bactericidal Efficiency of Menthol and Camphor. L. Gershenfeld and R. E. Miller. (*Amer. J. Pharm.*, 1933, **105**, 490–502.)—No bactericidal action could be attributed to either menthol or camphor when used as 1 per cent. solutions, either separately or mixed, but a saturated solution of menthol proved bactericidal against *B. typhosus* within 30 minutes (0·1 ml. of culture) and against *Staphylococcus aureus* (0·1 ml. of culture) within 24 hours in most instances, and bacteriostatic action was shown against *B. coli*. Saturated aqueous camphor solutions were less active and proved bacteriostatic only against *B. coli*, and neither bactericidal nor bacteriostatic against *B. typhosus* or *Staphylococcus aureus*. Solutions of menthol and camphor in a solvent composed of 31 parts each of alcohol, glycerin and water and 6·6 parts of soap, when tested against *B. typhosus* and *Staphylococcus aureus*, yielded the following phenol coefficients for menthol and camphor:—Average phenol coefficient with *S. aureus*: menthol, 1·2 at 37° C., compared with phenol at 20° C.; camphor, 0·5 at 20° C., compared with phenol at 20° C. With *B. typhosus*: menthol, 5·6 at 20° C., compared with phenol at 20° C.; camphor, 0·74 at 20° C., compared with phenol at 20° C. D. G. H.

Water Analysis

Occurrence of Hydrogen Phosphide in Well Waters. O. Lüning and K. Brohm. (*Z. Unters. Lebensm.*, 1933, **66**, 460.)—The occurrence of hydrogen phosphide in a well water was previously (*ibid.*, 1931, **61**, 443) attributed to the penetration of juice from sugar-beet slices or leaves into the sub-soil. Two similar cases have now been observed, but in these the odour soon disappeared.

T. H. P.

Agricultural

Feeding Value of Tung-Seed Meal. W. Godden. (*Bull. Imp. Inst.*, 1933, **31**, 352–358.)—Tung-seed was extracted below 45° C. with petroleum spirit (b.pt. 90°–105° C.), and the meal washed, dried, steamed for 40 minutes, and dried for 24 hours at 20°–30° C., giving sample A. On expressing the seed 24 per cent. of oil still remained, and the cake was therefore treated with solvent as above, and sample B was produced. Analysis of samples A and B gave the following percentage figures:—Moisture, 9·53, 10·47; crude protein, 28·12, 32·19; ethereal extract, 1·58, 0·57; crude fibre, 19·93, 22·04; total ash, 5·07, 5·73; soluble carbohydrates (by diff.), 35·77, 29·00; acid-insoluble ash, 0·23, 0·27; lime (CaO), 1·70, 0·83; soda (Na_2O), 0·066, 0·066; potash (K_2O), 1·27, 1·50; phosphoric acid (P_2O_5), 1·51, 1·82; chlorine, 0·029, 0·035; iron, 0·019, 0·016. Palatability and feeding trials were carried out with sample A; rats on a diet consisting of 25 per cent. of tung meal and 75 per cent. of their ordinary ration had begun to lose condition in 21 days, and did not eat very freely; poultry would hardly touch a mash containing as little as 5 per cent. of tung meal; cows, after the first time, refused 10 per cent.

in their production concentrates. Extended experiments were carried out with pigs, but under no condition did the pigs receiving tung-seed meal do well. *Post-mortem* examination of slaughtered types of the feed groups showed that some irritant material is present in the meal which has a harmful effect on the mucous membranes of the intestine. D. G. H.

Organic Analysis

Acetamide as a Solvent. O. F. Stafford. (*J. Amer. Chem. Soc.*, 1933, **55**, 3987–3988.)—Acetamide fuses at about 80° C. to a fairly mobile liquid, which appears to have a wider range as a solvent than any other substance investigated. About 400 organic and 200 inorganic compounds were tested; of the former, only cellulose was apparently quite unaffected. Asparagin, barbituric acid, oxamide, and uric acid (all slightly soluble in water and insoluble in alcohol and ether) are sparingly soluble below 100° C. Other organic ammonia derivatives, carbohydrates, alcohols, nitro- and nitroso-compounds, hydrocarbons, and acids are quite soluble. The solubility of inorganic compounds in acetamide is strikingly similar to their solubility in water; potassium perchlorate, the halides of mercury and lead, and mercuric oxide are more soluble in acetamide. Sparingly soluble inorganic compounds were precipitated, as in water, by double decomposition reactions. Bismuth nitrate gives a "basic" salt as a white precipitate. Mercurous nitrate and halides undergo some alteration; chromic acid and chromates are rather slowly reduced. W. R. S.

Rapid Determination of Mercaptans. G. R. Bond. (*Ind. Eng. Chem., Anal. Ed.*, 1933, **5**, 257–260.)—The method, which is applicable to impure gasoline, etc., involves titrating the sample with a solution of cupric oleate, when the mercaptans are precipitated according to the equation $4R\text{SH} + 2\text{Cu}(Ol)_2 = 2\text{CuS}R + R_2\text{S}_2 + 4\text{H}(Ol)$. Cupric oleate for the titrating solution was prepared by exactly neutralising "elaine" oil with sodium hydroxide, and treating it in warm dilute solution with the theoretical amount of cupric nitrate; the precipitated cupric oleate was dissolved in kerosene free from oxidation products, to give a solution containing about 4 grms. of copper per litre, and the solution was standardised by shaking a known amount with dilute hydrochloric acid to remove the copper, which was determined iodimetrically. The sample of gasoline to be tested, contained in a glass-stoppered cylinder, is titrated with the copper solution, with shaking. At the end-point a pale green colour of the solution, marking an excess of copper, becomes visible, and may be verified in the presence of much precipitate by filtering some of the liquid. The amount of copper solution required to produce a similar green colour with a sample of the gasoline, after extraction with alcoholic potash to remove mercaptans, should be deducted from that used in the mercaptan titration; 1 grm. of copper = 1·009 grm. of mercaptan sulphur. Hydrogen sulphide interferes, but may be removed, without seriously altering the mercaptan-content, by extraction with acidified cadmium chloride solution (Faragher, Morrell and Monroe, *Ind. Eng. Chem.*, 1927, **19**, 1281). The method was tested, with reasonably good results, on synthetic solutions of various mercaptans in naphtha. S. G. C.

Colorimetric Detection of Trichloroethylene, Carbon Tetrachloride and other Aliphatic Chlorinated Hydrocarbons in Technical Solvents. H. H. Weber. (*Chem.-Ztg.*, 1933, 57, 836.)—The method is based on the use of carbon tetrachloride by Driver (*Z. anal. Chem.*, 1930, 81, 62) for the distinction of α- and β-naphthols, and is more selective than existing reactions. Three tests are suggested, 1 drop of the sample being heated at the boiling point for 25 seconds with a small particle of sodium hydroxide (double quantity for ethylene dichloride) and (*a*) 2 ml. of a 2 per cent. solution of α-naphthol in cyclohexanol, or (*b*) cyclopentanol. The mixture is then transferred to another test-tube and cooled, the colour is noted, and an equal volume of (1) 85 per cent. sulphuric acid or (2) glacial acetic acid is added as a layer; after 1 minute the mixture is shaken and the colour is again noted. (*c*) In the neck of a test-tube (180 × 20 mm.) containing 2 drops of the sample, 2 ml. of a 2 per cent. solution of phenolphthalein in cyclohexanol, and a small particle of sodium hydroxide, is fitted an ordinary test-tube through which running water flows (to serve as a condenser), and the whole is immersed in a 200-ml. Erlenmeyer flask containing 30 ml. of boiling glycol. Exactly 5 minutes after the contents of the tube have started to boil the mixture is transferred to an ordinary test-tube and is cooled and shaken well with 1 ml. of glacial acetic acid and a few glass beads. The resulting colours are summarised as follows for solvents having b.pts. in °C. as shown:

Methylene chloride (40 to 60° C.)	Tech. acetylene dichloride		Chloroform (61° C.)	Carbon tetrachloride (77° C.)	Ethylene dichloride (81° to 87° C.)	Trichloroethylene (85° to 87° C.)	Tetrachloroethylene (119° to 120° C.)	Tetrachloroethane (144° C.)	Pentachloroethane (159° C.)
	48·5° C.	60° C.							
Blue	Yellow-brown	Yellow-brown	Blue	Blue	Yellow-brown	Yellow-brown	Yellow-brown	Grey	Brown
Green-blue	Reddish-violet	Violet	Intense blue	Intense blue	Colourless or very weak green	Intense green-blue	Green	Intense green-blue	Grey-green
Yellow	Yellow	Colourless	Orange yellow	Red	Colourless	Yellow tinge	Colourless	Yellow tinge	Yellow
Yellow tinge	Yellow tinge	Yellow tinge	Yellow tinge	Light brown	Yellow tinge	Green	Yellow tinge	Green	Yellow tinge
Colourless	Almost colourless	Almost colourless	Reddish-brown	Reddish-brown	Lilac	Almost colourless	Almost colourless	Lilac-red	Colourless

The minimum percentage quantities detectable in petroleum spirit and in benzene, respectively, are:—Methylene chloride, 0·1, 0·5; acetylene dichloride (b.pt. 60° C.), 10·0, 10·0; chloroform, 0·1, 0·1; trichloroethylene, 1·0, 2·5; tetrachloroethane, 0·1, 5·0; carbon tetrachloride, 0·05, 0·1 [by reagent (*a*1)]. Chloroform, 0·5, 0·5; carbon tetrachloride, 0·1, 0·5 [reagent (*a*2)]. Trichloroethylene, 15, 15; tetrachloroethane, 20, 15 [reagent (*b*)]. Ethylene dichloride, 75, 75; tetrachloroethane, 75, 75 [reagent (*c*)]. J. G.

New Method for the Differentiation and Determination of Formaldehyde and Acetaldehyde in their Mixtures. M. V. Jonescu and H. Slusanschi (*Bull. Soc. Chim.*, 1933, 53, 909–918.)—Investigation of the rates of reaction of formaldehyde and acetaldehyde with dimedone (dimethyl dihydroresorcinol) affords a means of distinguishing between the two aldehydes and of determining them when mixed. With solutions of each aldehyde, the times which elapse before a precipitate is formed with dimedone depend on the concentration of the aldehyde, and these times have been determined for concentrations ranging from *N*/5 to *N*/7500. From the time-concentration curves the concentration of either aldehyde in its pure solution may be read off directly. This method is quicker and more exact than the titrimetric, gravimetric or colorimetric methods available.

The curves show that there is a definite concentration (*N*/150) below which the time necessary for the appearance of a precipitate with acetaldehyde exceeds the 75 minutes necessary for completion of the precipitation with formaldehyde. If, at this concentration of aldehyde, precipitation occurs 4 minutes 45 seconds after addition of the reagent, only formaldehyde is present, but if the time is between this and 75 minutes, the solution contains both aldehydes, and the proportions of the two are given by the time reading. If the time is 75 minutes, acetaldehyde only is present.

With the *N*/150 formaldehyde solution, the time of precipitation is short, and, to diminish the error involved in measuring the time, it is recommended that a concentration *N*/225 be used. As addition of the reagents dilutes the solution three-fold, the aldehyde solution tested is made of *N*/75 strength. The procedure is as follows:—

The total aldehyde concentration of the solution is determined by Ripper's iodimetric method (*Monatsh.*, 1900, **21**, 1079), the solution being treated with excess of standard potassium bisulphite solution, and the excess determined by titration with iodine solution. The aldehyde solution is then diluted to *N*/75 strength, and 5 ml. are placed in a test-tube with 10 ml. of dimedone solution (6 grms. per litre); the tube is inverted to effect mixing and the stop-watch started at once. As soon as crystalline precipitate appears, the watch is stopped. The percentage concentrations of the two aldehydes in the solution, as diluted by the reagent, are shown in the following table:

Time of precipitation		Grms. per 100 ml.	
Min.	Sec.	Formaldehyde	Acetaldehyde
5	40	0·0066	—
6	0	0·0060	0·00098
6	40	0·0050	0·00244
8	0	0·0040	0·00391
9	30	0·0030	0·00538
11	50	0·0020	0·00684
14	0	0·0015	0·00758
16	0	0·0012	0·00802
20	0	0·0010	0·00831
28	0	0·00075	0·00868
35	0	0·00060	0·00890
58	0	0·00030	0·00939
75	0	0·00020	0·00948

These values must be multiplied by 3 to obtain the contents of the aldehydes in the *N*/75 solution tested. The minimum percentage of formaldehyde thus determinable

accurately is 0·0006 (in the *N*/225 solution). If less than this is indicated, the test is repeated with a solution three times as strong, and the concentrations are then read off from the following table:

Time of precipitation		Grms. per 100 ml.	
Min.	Sec.	Formaldehyde	Acetaldehyde
2	20	0·020	—
3	20	0·015	0·00733
4	10	0·012	0·01173
4	45	0·010	0·01466
5	20	0·0075	0·01833
5	40	0·0066	0·01965
6	0	0·0060	0·02053
6	40	0·0050	0·02200
8	0	0·0040	0·02346
9	30	0·0030	0·02493
11	50	0·0020	0·02640
14	0	0·0015	0·02713
16	0	0·0012	0·02757
20	0	0·0010	0·02786
28	0	0·00075	0·02823
35	0	0·00060	0·02845
58	0	0·00030	0·02889
75	0	0·00020	0·02904

The laboratory preparation of dimedone is described. T. H. P.

Determination of Higher Alcohols (Fusel Oil). B. Bleyer, W. Diemair and E. Frank. (*Z. Unters. Lebensm.*, 1933, **66**, 389–395.)—Of various aldehydes tested as substitutes for the salicylaldehyde usually employed in the colorimetric determination of fusel oil in alcohol by Komarowsky's reaction, *p*-dimethylaminobenzaldehyde has proved the most suitable, and offers certain advantages over salicylaldehyde. T. H. P.

Characterisation of Sansa [Olive] Oil. F. Bernardini and E. A. Gauthier. (*Giorn. Chim. Ind. Appl.*, 1933, **15**, 329–330.)—Morawski's reaction (with acetic anhydride and sulphuric acid) and Pettenkofer's reaction (with alcoholic furfural solution and sulphuric acid) are given, not only by the resins of sansa oil, but also by the phytosterols found in all vegetable oils. The sterols may be removed by the following procedure: Twenty ml. of the oil are heated to boiling with 20 ml. of 70 to 75 per cent. (by vol.) alcohol, and the cooled liquid is filtered through a paper moistened with alcohol. The filtrate is evaporated to dryness in a dish, and the residue is heated with 15 ml. of 2 *N* potassium hydroxide solution on a water-bath to saponify the resins. The alkaline liquid is then extracted with ether, which dissolves out the phytosterol. To ascertain when this extraction is complete, 3 ml. of concentrated sulphuric acid are poured carefully down the side of a test-tube containing 5 ml. of the separated ethereal solution, and 10 drops of a 0·25 per cent. solution of furfural in alcohol; when the acid is cautiously mixed into the solution, at most a faint pink colour should appear.

When this is the case, the alkaline solution, containing only the resins, is acidified with 3 ml. of concentrated hydrochloric acid, and the resin acids thus liberated are extracted with about 20 ml. of ether. About 5 ml. of the ethereal solution are used for the furfural and sulphuric acid test, and the remainder is evaporated to give a residue to which the acetic anhydride (3 drops) and sulphuric acid (1 drop) test is applied; the latter test gives a violet-red, and the former an amethyst-violet, colour with resins. A fresh sample of olive oil gave no colour with either test, but two old oils (3 years and 1 year), containing respectively 13·54 and 3·95 per cent. of oleic acid, gave a deep violet colour changing to reddish-brown with the Morawski test and a deep reddish-brown changing to deep violet with the Pettenkofer test. Five sansa oils, some old and some fresh, were tested, and all showed a violet-red colour with the Morawski test, and an amethyst-violet colour with the Pettenkofer test. T. H. P.

Colour Reactions of Meta-dinitrobenzene in Alkaline Solution. R. Truhaut. (*J. Pharm. Chim.*, 1933, **125**, 339–353.)—The aldehydes and ketones examined gave a colour reaction with *m*-dinitrobenzene in alkaline solution, although in some cases it was necessary to apply heat. The reaction appears to be a general one, but no colour was formed with camphor. Acetone gives a positive reaction, and with denatured alcohol a pink colour turning brown was observed. This reaction might prove useful to detect (after distillation) adulteration of tinctures with denatured alcohol. The reactions of compounds containing a CO group were also examined, 1 ml. of a 1 per cent. alcoholic solution of *m*-dinitrobenzene and 2 ml. of 10 per cent. sodium hydroxide solution being used, and 0·1 grm. of the compounds added to the warmed mixture. Uric acid alone gave a positive reaction, yielding a very stable and characteristic violet colour. With certain amino acids (glycocoll, lysine and β-alanine) a violet ring is formed when 2 ml. of 1 per cent. alcoholic *m*-dinitrobenzene solution are poured, without mixing, on to a solution of 0·1 grm. of amino acid in 2 ml. of 10 per cent. soda solution, and the mixture is very lightly shaken. The reaction is most pronounced with glycocoll, and is enhanced if the glycocoll is dissolved in the *m*-dinitrobenzene and a few solid pieces of the alkali are added. Tryptophan gives a yellow colour, cystein and glutathione a yellow green colour, turning brown-black; phenyl β-alanine gives a brown colour, rapidly changing to an intense violet. D. G. H.

Inorganic Analysis

New Colour Reactions of Cuprous Salts. G. Tartarini. (*Gazz. Chim. Ital.*, 1933, **63**, 597–600.)—Cuprous salts give deep red colorations and orange precipitates with $\alpha\alpha$-dipyridyl, and violet colorations and blue precipitates with *o*-phenanthroline. In this preliminary paper the characteristics and compositions of four of the compounds thus formed are described. T. H. P.

Determination of Tin by Means of Phenylarsonic Acid. J. S. Knapper, K. A. Craig, and G. C. Chandlee. (*J. Amer. Chem. Soc.*, 1933, **55**, 3945–3947.)—Phenylarsonic acid (which is known to precipitate zirconium and thorium) can be used for the quantitative determination of tin. Metallic tin (about 0·1 grm.), or one of its alloys, is attacked with nitric acid, after which the excess acid is driven off without dehydration of the stannic acid. Strong hydrochloric acid is then added, drop by drop, until the precipitate dissolves. The solution is diluted to 150 or 200 ml., which should provide for a maximum acidity of 5 volumes per cent. of strong hydrochloric acid. The hot solution is treated with 35 ml. of a saturated aqueous solution of the reagent. Under the proper conditions of acidity the precipitate can be collected after a very short time, but near the prescribed maximum acidity the solution should stand for several hours; a little pulp assists filtration. The precipitate is washed with 4 per cent. ammonium nitrate solution until free from chlorides or sulphates, and ignited gently until the paper is charred. It is then heated in an electric furnace at about 1100° C. to constant weight. None of the metals occurring in brass or bronze is occluded in the precipitate, with the exception of iron. If this is present, the washed precipitate is dissolved in about 5 ml. of strong hydrochloric acid, the solution is diluted to about 200 ml., and the precipitation is repeated. W. R. S.

Solubility of Lead Chromate. M. Huybrechts and C. Degard. (*Bull. Soc. Chim. Belge*, 1933, **42**, 331–346.)—The solubility of lead chromate in various reagents at 20° C. was determined. The figures below indicate grms. of $PbCrO_4$ per litre of solvent. Water dissolves 0·00017 grm.

Acetic acid		Ammonium acetate		Acetic acid (*a*) + amm. acetate (*b*)		Potassium chromate	
0·025 *N*	: 0·00130	0·05 *N*	0·00093	(*a*) 0·1 *N* (*b*) 0·05 *N*	0·00175	0·1 *N*	*nil*
0·05 *N*	: 0·00234	0·1 *N*	0·00136			0·01 *N*	*nil*
0·1 *N*	: 0·00429	0·2 *N*	0·00210	(*a*) 0·2 *N* (*b*) 0·05 *N*	0·00234	0·001 *N*	*nil*
0·2 *N*	: 0·00468	0·5 *N*	0·00936			0·0002 *N*	0·000,006
0·5 *N*	: 0·00616						

The solubility in 0·1 to 0·04 *N* solutions of calcium chromate is so slight that it could not be determined. The presence of calcium ion favours the flocculation of lead chromate. The following solubilities were observed in 0·004 *N* calcium chromate solutions containing also:

Ammonium acetate		Acetic acid	
0·2 *N*	0·00004	0·2 *N*	0·00004
0·1 *N*	0·00002	0·1 *N*	0·000015
0·05 *N*	0·00002	0·05 *N*	0·000015
		0·02 *N*	0·000015

In solutions containing ammonium acetate, acetic acid, and calcium chromate at concentrations similar to the above, the solubility was of the order of 0·00002 grm. Neutral lead chromate may be precipitated from cold, neutral nitrate solution by potassium chromate in presence of 20 ml. of 0·01 *N* calcium nitrate solution. A measured excess of chromate being used, the excess may be determined in the filtrate by iodimetry. W. R. S.

Detection of Caesium, Rubidium and Thallium. P. Robin. (*J. Pharm. Chim.*, 1933, **12**, 384–387.)—The following process, which involves concentration of the rare metal salts and subsequent spectroscopic examination, has been used for mineral waters: Two litres or more of the water are concentrated to a small volume, and one-tenth each of this volume of acetic acid and of sodium cobaltinitrite reagent (28·6 grms. of anhydrous cobalt nitrate, 180 grms. of sodium nitrite, 1000 ml. of water, together with 50 grms. of glacial acetic acid) are added, in order to precipitate the potassium, caesium, rubidium, and thallium as triple nitrites. After being kept for 24 hours at a low temperature the precipitate is filtered off, washed with acetic acid (10 per cent.) and dried. The precipitate is decomposed by heating at 300° to 350° C. in a metal capsule, yielding cobalt oxide and the nitrites of sodium, potassium, etc. The residue is extracted with water, and the cobalt oxide is filtered off, washed, and rejected. The solution is acidified with hydrochloric acid and evaporated to dryness on a water-bath. The dry chlorides are dissolved in 4 parts (by weight) of water, and the solution is diluted with 2·5 volumes of alcoholic hydrochloric acid [1 vol. of hydrochloric acid (22° Bé.) and 2 vols. of alcohol (96 per cent.)] resulting in precipitation of the bulk of the sodium and potassium chlorides, which are removed by filtration and rejected. The filtrate is evaporated, and this separation process is again applied. The solution containing the rare metals is evaporated with an excess of nitric acid in order to convert the chlorides into nitrates. The dry nitrates are dissolved in 15 parts of water, and an equal volume of freshly prepared silver and bismuth nitrite reagent [5 ml. of sodium nitrite solution (50 per cent.), 1 ml. of bismuth nitrate solution (50 per cent.), 2 ml. of silver nitrate solution (10 per cent.)] is added; caesium, rubidium and thallium are precipitated (the limiting concentration for precipitation by the reagent is 6×10^{-2} for potassium, and 1×10^{-5} for caesium, indicating the necessity for removal of potassium as far as possible by the alcoholic hydrochloric acid process). The bismuthinitrites of caesium, rubidium and thallium crystallise in yellow rectangular plates. After the liquid has stood 24 hours at a low temperature the precipitate is filtered off on a sintered glass funnel and washed with alcohol. It is then dissolved in a few drops of nitric acid, which is evaporated off, and the residue is dissolved in 1 ml. of water. Spectroscopic tests are then made for the rare metals, a little of the solution absorbed in a cotton fibre wound around a platinum wire being used for introduction into the flame. S. G. C.

Analysis of Clays. R. C. Groves. (*J. Agric. Sci.*, 1933, **23**, 519–525.)—Alternatives to the sodium carbonate fusion method have been investigated. The following method, involving decomposition of the sample with "tri-acid" mixture, was found to be satisfactory for the determination of silica, alumina, iron oxide and titania in most soil clays: To 1 grm. of the clay are added 50 ml. of acid mixture [150 ml. of sulphuric acid (sp.gr. 1·84), 300 ml. of hydrochloric acid (sp.gr. 1·2), 100 ml. of nitric acid (sp.gr. 1·42), and 450 ml. of water]. The liquid is heated to boiling, and when nitrous fumes have ceased to be evolved, it is evaporated until fumes of sulphuric acid are given off. The residue is cooled, dissolved, as far as possible, in 100 ml. of water, and the silica is filtered off; traces of silica in the filtrate are recovered by a second evaporation process. The silica is ignited, weighed, and evaporated with hydrofluoric acid and sulphuric acid in the usual way; the residue is fused with potassium bisulphate, and the melt is dissolved in water and added to the main filtrate. Titania may be directly determined colorimetrically in the filtrate after addition of hydrogen peroxide. The liquid is subsequently boiled to decompose the peroxide, and divided into two equal parts. In one part of the solution, after the addition of 20 ml. of hydrochloric acid, the "total sesquioxides" are precipitated by means of ammonia, filtered off, ignited and weighed. In the other part the iron and titanium are precipitated by the addition of sufficient sodium hydroxide to keep the aluminium in solution, the object being to remove the bulk of the aluminium. The precipitate is filtered off and dissolved in dilute sulphuric acid; the solution is neutralised with ammonia, and diluted to 300 ml., 30 ml. of hydrochloric acid are added, and the liquid is cooled. The iron and titanium are then precipitated by means of cupferron in the usual way, and the precipitate is ignited. The weight of iron oxide is obtained by deducting the corresponding amount of titania found from the colorimetric determination, and the weight of alumina is obtained by deducting the combined weight of iron oxide and titania from the weight of the "total sesquioxides." Some clays, notably those with a high silica : alumina ratio, or clays which have been ignited before analysis, are not completely decomposed by acid, and the sodium carbonate fusion process is necessary. Incomplete attack of the clay by the acid mixture is revealed by an abnormally high residue being left after the usual hydrofluoric acid volatilisation of the silica. S. G. C.

Microchemical

Quantitative Drop Analysis. (I) Apparatus and Technique. P. L. Kirk. (*Mikrochem.*, 1933–34, **14**, 1–14.)—Apparatus is described for micro-volumetric work suitable for volumes of 0·5 ml. down to a fraction of a drop. *Pipettes* of volumes ranging from 0·01 ml. to 0·2 ml. are made from glass capillaries, in the ends of which are sealed, with Krönig cement, fine hypodermic needles. The liquid measured is controlled by a 0·5-ml. tuberculin syringe. The same syringe may be used for a series of pipettes. *Vessels for titration and precipitation.*—For small volumes a microscope slide is used; for larger volumes a depression, which is preferably frosted, in a thick slide. When heating is necessary a conical glass vessel, about ⅜ inch in diameter, is used, a small handle for this being made by sealing to the edge a thin glass rod. When the volume is very large, casserole-shaped vessels of 0·5 to 1·0-ml. capacity are used. *Stirrer.*—An electric stirrer is made from an electro-magnet, such as is used in a small electric buzzer; this is attached to the side of a small wooden block, and in the adjacent side of the block a glass tube is inserted and bent round to pass in front of the magnet cone, at a distance of about 2 mm. At the point nearest to the magnet a small piece of iron is sealed inside the glass tube. The glass tube is drawn out, and therefore made flexible between the place of insertion and the electro-magnet; it is wider at the point where the iron is placed, and then drawn out to a very fine tip, which is bent down slightly to form the stirrer. The current from a 110-volt alternating circuit is passed through the electro-magnet, an electric light bulb in circuit being used to give the necessary resistance. The stirrer vibrates according to the frequency of alternation (usually 60 cycle). Either a tapping switch (for momentary stirring) or an ordinary switch is used. *Burettes.*—Three types are used, all of which are made from thick-walled capillary tubing of about 0·5 mm. bore, and readings are accurate to about 0·02 to 0·03 c.mm. In the first type the titrating solution is on the top of a mercury thread which is raised by a steel screw.

The top of the burette is bent over in the form of an inverted U-tube. A small reservoir at the top of the U-tube facilitates refilling. There is a removable tip attached with rubber cement and fixed outside by means of 2 brass collars with an open-sided coupling between them to draw the collars together. The capacity is made 0·1 to 0·2 ml. The only disadvantage occurs when a titrating solution oxidises the mercury. The second burette is made in the same way as the pipettes, except that a screw is used to depress the plunger, and a coil spring is used to prevent backlash. The scale used is cut from graph paper. There is a slight lag due to compression or expansion of the air in the burette and syringe. The third burette is a combination of the two types, but a bubble of air in a small bulb in the capillary separates the titrating liquid from the mercury. The burettes are calibrated by measuring the length of a short thread of mercury over successive intervals to find the variation in bore of the tube, then the mercury-content of the burette is weighed, and finally the water-content, to find the drainage error, which is usually small. An adjustable titration table should be used for the work. *Heating equipment.*—An electric cigar lighter is a useful hot plate. A micro water-bath is made from a glass bulb of about 1½ in. diameter, heated with a small electric coil. *Filtration apparatus.*—Transfer of precipitate is generally impracticable. The filtrate can be transferred by filtering the liquid through a fine capillary with the end flared to hold either a 0·5-cm. sintered glass disc or a little asbestos. The filtrate is collected in a micro suction-flask of about 3-ml. capacity. *Centrifuge.*—A centrifuge is adapted or constructed to centrifuge the contents of tubes of about 0·5-ml. capacity. Titrations may be carried out with an accuracy of 0·2 to 0·3 per cent. The apparatus should be especially useful in chemical and biological work.

J. W. B.

Quantitative Drop Analysis. (II) Determination of Calcium. R. P. Mitler and P. L. Kirk. (*Mikrochem.*, 1933–34, **14**, 15–22.)—For simple solutions containing calcium the sample is measured with a syringe pipette into a conical glass vessel (see preceding abstract), and the pipette is rinsed once, the rinsing water being added to the sample. An equal volume of approximately saturated ammonium oxalate solution is then added, the mixture being stirred during the process. The vessel is heated over the micro hot plate until steam is evolved, ammonia is then added in slight excess, the digestion is continued for a few minutes, and the mixture is left for half an hour, after which it is filtered through the sintered glass filter. If this has been found not to retain the precipitate, it must be treated with a very small amount of asbestos suspension, prepared so as not to give a blank with permanganate. The precipitate is washed dropwise with dilute ammonia (1:6), which has been saturated with calcium oxalate before use. From 3 to 6 washings are sufficient. The precipitate is then dissolved in a drop of 2 *N* sulphuric acid, and another drop on the filter disc. The capillary burette (the second or third type described in preceding abstract) is filled with 0·01 or 0·05 *N* potassium permanganate solution, and the mixture is titrated while on the water-bath; a magnifying glass is useful to observe the end-point. When the end-point is nearly reached a minute crystal of diphenylamine is added, and the titration is continued until the appearance of the blue-violet colour. For blood serum or plasma, about 20 c.mm. of the sample, containing about 5γ of calcium, is taken. It is usually necessary to clarify by centrifuging before taking the sample. The precipitation is carried out in the cold, and no ammonia is added. Immediately before filtration the mixture is diluted five times with water; this reduces the viscosity of the serum, rendering filtration less difficult. With serum it appears to be necessary to use asbestos on the filters. The method has been tested on known solutions of calcium chloride, on ox serum and on blood, with errors of less than 1 per cent. J. W. B.

Microchemical Soil Tests. M. F. Morgan. (*Conn. Agri. Exp. Station* (*New Haven*) *Bull.*, No. 333, 1932, 111–132.)—Simple soil tests for small samples, suitable for field or laboratory tests, include p_H, available phosphorus, nitrate nitrogen, ammoniacal nitrogen, replaceable calcium, and active aluminium. The tests are approximately quantitative. The small sample of soil for testing must be taken from a well-mixed field sample of ordinary-size, collected from 6 to 20 different points in the plot under examination. All the tests make use of the porcelain Morgan Soil-Test Block for washing a few drops of the soil solution out of the soil. The block is made for three separate samples of soil. The soil is placed in a small depression separated from a channel by a perforated section of porcelain through which the solution filters down and collects in a second depression at the other end of the block. The block is sloped so that the soil sample is higher than the depression in which the soil solution collects. To prevent the soil passing through the perforations, clean quartz sand may be placed at the other side, except for a sample to be used for the phosphate test. *Hydrogen ion test.*—The leaching liquid is a 0·3 per cent. (0·05 *N*) solution of sodium chloride. Three samples of soil are placed in the compartments of the Morgan block and a small drop of one of 3 different indicators is placed in each of the wells at the other end of the block. The leaching liquid is then dropped slowly on to the soil until it becomes saturated. From the colour-change of the indicators as the soil solution percolates into the different well depressions, the p_H may be determined. Indicators used were bromthymol blue (0·04 per cent.), 6·0–7·6 p_H range; chlorophenol red (0·04 per cent.), 5·0–6·6 p_H range; and bromcresol green (0·04 per cent.), 3·8–5·4 p_H range. For special work, bromphenol blue, cresol red and thymol blue are used. Colour charts are used.

Nitrate nitrogen.—The leaching liquid is distilled water. The reagent is made from 0·05 grm. of diphenylamine in 2·5 c.c. of concentrated sulphuric acid, and kept in a dark bottle at a low temperature. One drop of the extract-solution and 4 drops of the reagent solution are used, and the colour is compared with that of the chart (given in the Bulletin), or with that given by a standard nitrate solution. Nitrate in plant material may be similarly determined by leaching the sample with a few drops of water in the Morgan Block.

Ammoniacal nitrogen.—The leaching solution is a saturated solution of potassium chloride, and the reagent is Nessler's reagent. Four drops of the soil-extract are used in the spot plate with 1 drop of the reagent, and the colour is compared, as before, with a chart or a standard. J. W. B.

Reviews

A SHORT MANUAL OF SYSTEMATICAL QUALITATIVE ANALYSIS BY MEANS OF MODERN DROP REACTIONS. By Prof. Dr. C. J. VAN NIEUWENBURG and Miss IR. G. DULFER. Pp. 88. Amsterdam: D. B. Centen's Uitg. Maatschappij (N.V.).

The well-known linguistic capabilities of the Dutch are illustrated by the present volume, which has been written in English by two members of the chemical staff of the Technical University at Delft. The evidence for their independence of English assistance, which runs like a thread throughout the text, consists of unusual spelling, quaint phrases, in certain expressions a meticulous grammatical accuracy that appears strange to us who by long familiarity have grown careless, and finally a rather novel use of exclamation marks to emphasise sentences.

The volume is intended as a practical qualitative manual for the use of students and analysts, and the principle adopted throughout is semi-microchemical in character, and one in which the test-tube and filter are largely replaced by a porcelain drop-plate or microscopic slide and a centrifuge. By this means the expedition, certainty, and economy of material of the more recently developed method are attained, and a student is enabled to detect from 5 to 10 cations in a quantity of material between 100 and 300 milligrammes in weight.

After some general remarks containing much excellent advice, the analytical reactions of the commoner metals and acids are given, and these are followed by Chapter III, dealing with the so-called "rare" elements, which the authors rightly state are often common, but are deceptively kept in the background, since they give much trouble in analysis. In the next section the dry, and other preliminary tests, are given in full detail and, although these are decried by some teachers, they undoubtedly provide excellent training for the student, and are of considerable value in later work. The next 15 pages contain the separation scheme for practically the whole of the metals, and, although so comprehensive, it appears thoroughly reliable. In this connection it is of interest to notice that the authors have found none of the newer methods of separation equal in reliability to the old and well-tried hydrogen sulphide method, and most of us will agree with them. In Chapter VI, fuller details of manipulation of the drop reactions mentioned earlier in the text are given, the book being brought to a close with a bibliography of original papers, etc., and a list of the reagents required.

The volume is not intended for use in the detection of traces of elements, and contracted methods, often untrustworthy, are not suggested; it has, however, many merits as a manual for use in the more modern methods of analysis and, in spite of some minor defects, is an excellent production. The authors deserve commendation for their courage in the production of such a textbook in a language which to them is foreign, and still more for the undoubted success they have achieved. The suggestion may, however, be made that the proofs of future editions should be submitted to an English chemist for revision, in order to eliminate the continental spelling and modes of expression.

T. J. WARD

WATER PURIFICATION CONTROL. By EDWARD S. HOPKINS. Pp. ix+131. London: Baillière, Tindall & Cox. Price 10s.

This little book, by the principal sanitary chemist of the Bureau of Water Supply, Baltimore, Maryland, is evidently the fruit of much experience and shrewd observation. It should be useful to both waterworks engineers and chemists, and to those consultants who deal with problems of water purification. The writer of the foreword, Abel Wolman, described it as "designed, in simplicity of language and arrangement, to meet the needs of the rank and file." The arrangement is both good and simple, and, as the author usually uses short sentences, the language is, in a way, simple and, when dealing with practical matters, clear. The book, however, is full of inelegant sentences, such as:—"The p_H test is very accurate, is not unduly influenced by atmospheric conditions and, upon addition of acid, alkali or buffer salts, becomes quickly stabilised." "The clarity of filtered water should not exceed 0·2 to 0·5 p.p.m. of turbidity." "Use of ammonia to form chloramines with chlorine has been extensively utilised." If the reader knows something about the subject, it is always possible to know what Mr. Hopkins means, and he is usually right, but more precise language would have been equally simple, and at least as attractive to the rank and file.

It is interesting to note that storage appears to play no part in water purification in the United States, as expounded by this author. The water supply in some of the western States is so uncertain that one has seen suggestions that highly purified sewage should be conserved, and yet only methods which are applicable to the rapid treatment and distribution of water are described in this work.

In discussing coagulation of matters causing turbidity and the removal of colour, the author rightly stresses the importance of p_H control. He shows that, whereas matters causing turbidity are best removed, when alum is used as precipitant, if the p_H is adjusted to from 5·7 to 7·4, colour can be removed best at a p_H well on the acid side of neutrality, lime being added after coagulation to reduce the corrosive action of the treated water. A new and favourite coagulant, which is attracting some attention in this country, is "chlorinated copperas"—$Fe_2(SO_4)_3$, $FeCl_3.7H_2O$. The discussion of coagulation is very good, and filtration, disinfection (chlorination), tastes and odours and corrective treatment to reduce corrosion, receive sufficient attention. Useful tables, graphs, report forms, and a nomogram for determining chlorine dosage add to the value of this work.

The book is well and clearly printed on good paper, but the price seems excessive. Should it reach a second edition, as it deserves, the author would be well advised to revise the text, after a course of, say, the Bible or Defoe, both examples of simple writing for the rank and file. J. H. COSTE

THE PHARMACY AND POISONS ACT EXPLAINED. By H. GLYN-JONES. With Introduction by H. P. LINSTEAD. Pp. 117. London: Eyre & Spottiswoode. 1933. Price 8s. 6d. net.

The passing of the Pharmacy and Poisons Act during this year is an important milestone in the history of pharmacy, and for all pharmacists and others, who in any way handle pharmaceutical products, a thorough understanding of this Act is essential. From both the pharmaceutical and the legal aspect, Mr. H. Glyn-Jones possesses all the necessary qualifications for elucidating the official phraseology of the Act, and in this he has succeeded, in a volume of just over one hundred pages.

It must be remembered that, as it stands at present, the Act is merely the skeleton around which the edifice must be built. It is not a Consolidating Act, and how and when such an Act or Acts will be passed in order to complete the scheme, is a matter for the future; but already there is abundant evidence that the regulations governing the practice of pharmacy are to undergo far-reaching changes.

From the point of view of the pharmacist, probably the most important changes are that membership of the Pharmaceutical Society—up to now voluntary—becomes compulsory, and that the conduct of his business comes under official control to a greater extent than at present.

For the Public Analyst there is one important item, and that is, that if a prosecution results from a breach of the Act, and the defendant does not question the Analyst's certificate, the Analyst himself need not be summoned to attend the Court.

The book is attractively arranged and free from errors. It will be required by all who wish to understand the changes taking place in the laws relating to pharmacy and poisons.

S. G. STEVENSON

ORGANIC AND BIO-CHEMISTRY. By R. H. A. PLIMMER, D.Sc. Fifth edition. Pp. x+624. London: Longmans, Green & Co., Ltd. 1933. Price 21s. net.

The fifth edition of Professor Plimmer's well-known hand-book of organic and bio-chemistry follows closely the lines of the previous editions, and the high standard which he has set hitherto is well maintained. Several additions have been made, and the subject-matter has been brought up to date. This book, as the author says in the preface, has become a fuller and more comprehensive course on the subjects dealt with, and for this reason the title has been changed from *Practical Organic and Bio-chemistry* to *Organic and Bio-chemistry.* The work is divided into fifty-seven chapters, and these deal with the chemistry of the aliphatic and aromatic compounds, proteins, colloids, milk, blood, metabolism, composition of foodstuffs, respiratory exchange, urine, faeces, hydrogen-ion concentration, etc.; a useful list of the commoner reagents is appended. As in previous editions, full details for the carrying out of suitable laboratory experiments are included.

Taken as a whole, the volume adequately fulfils the aims of the author, namely, to consider organic chemistry, not as a subject by itself, but as the basis of physiological chemistry. The author is to be congratulated on the way in which he has dealt with the material at his disposal. The volume may be thoroughly recommended and should meet the needs not only of the medical student, but also of first-year science students.

The book is well produced and is written in an interesting manner. The text is exceptionally free from mistakes, and the numerous diagrams and figures are clearly represented. The author, however, should never omit, as he almost invariably does, to place a zero before decimal fractions. Thus, for example, "$\cdot 1N$-H_2SO_4" should always read "$0\cdot 1N$-H_2SO_4." The book is well indexed.

R. H. SLATER

FEBRUARY, 1934 Vol. 59, No. 695

12. MAR. 1934

THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

Deaths

We greatly regret to have to record the deaths of the following members of the Society:

John Joseph Bryant.
John Haworth, on January 19th.
Thomas James Hutchinson.
William Marshall (Public Analyst for Stockport), on January 16th.
George Tate, on November 24th.

Obituary

WILLIAM PARTRIDGE

William Partridge was born in Westminster, was educated at the United Westminster (now Westminster City) School, and proceeded in 1897 to Finsbury Technical College with a Holl Scholarship. After completing the 3 years' course there he became assistant to the late William Chattaway, and after Chattaway's death joined Mr. C. G. Moor in private practice, but for a good many years past he had worked independently. Jointly with Mr. Moor he held the appointments of Public Analyst for the County of Dorset and the Boroughs of Poole and Penzance, was also Public Analyst and Official Agricultural Analyst for the County Borough of Burton-on-Trent, and for the past year had been Public Analyst for the Metropolitan Borough of Fulham. He also acted as temporary Public Analyst for the County of Cornwall for nine months after the death of the late Benedict Kitto. Another of his official appointments was that of lecturer on the Analysis of Food and Drugs at the South-Western Polytechnic, Chelsea, and also, at a later date, lecturer in Chemistry (Public Health) at King's College, London.

Apart from his official work, Partridge was engaged in analytical practice, and also devoted a good deal of time to private coaching and to literary work. His books include *Aids to Bacteriology*, *A Dictionary of Bacteriological Equivalents*, and *The Bacteriological Examination of Disinfectants*, but he will be chiefly remembered in this connection as the joint-author of *Aids to the Analysis of Food and Drugs*. The revision for the 4th edition, published in 1918, was almost entirely his work.

He joined the Society of Public Analysts in 1903, and was a very active member, serving on the Council in 1917–18 and 1928–29, and as Vice-President in 1930–31. He rarely missed the meetings at Burlington House, or the informal dinners which precede them, often took part in the discussions, and contributed several papers to the Society, and very many useful and practical "Notes" that were published in the ANALYST. Nothing gave him greater pleasure during the last few years of his life than serving on the Publication Committee of our Society.

With very decided opinions, odd prejudices, nervous hesitating speech and many quaint ways, Partridge possessed "personality" in a marked degree. No one could be a more loyal friend, and it was characteristic of him that he "went all out" in helping anyone to whom he was drawn by sympathy or some common interest.

A very severe attack of influenza in 1919 seriously affected the health of one who was never robust. It was noticed that he was not present at the meeting of the Society on December 6th of last year, and it came as a great shock to his many friends to learn that he had been taken ill on that day and had passed away on the 11th December, in his 53rd year. He leaves a widow, but had no children.

ERNEST M. HAWKINS

THE CHEMICAL (AS DISTINCT FROM PHYSIOLOGICAL) TESTS FOR VITAMINS

The following papers were contributed to the discussion on this subject at the meeting on November 1st,* 1933:

The Chemical Evaluation of the Vitamins

BY A. L. BACHARACH, M.A., F.I.C., AND
E. LESTER SMITH, D.Sc., F.I.C.

THE limitations set to the subject of this paper present an interesting paradox when the history of vitamin research is considered. In descending order of importance the methods that have been used for elucidating the properties of the vitamins, considered as a group, are the biological, the physical, and the chemical. Yet it is not intended here to consider biological methods at all, and physical methods will be discussed only in so far as they bear upon those that are more specifically chemical. We have thus to direct our attention to those properties that have been so far of least importance in advancing our knowledge.

That very paradox, however, carries with it considerable grounds for optimism. The fact that analysts are to-day able to discuss the chemistry of the vitamins suggests that we have advanced a very considerable distance along the road to their isolation and complete chemical identification.

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* For discussion see p. 98 *et. seq.*

There is a sense in which all biological tests are chemical, and all chemical tests biological. Every biological test itself depends upon a reaction, or a series of reactions, sometimes bewilderingly complex, taking place in the body of the experimental animal; a chemical test, whether gravimetric, volumetric, or colorimetric, must depend upon the observations of a chemist, and the chemist himself becomes an experimental animal used in the test.

It will be necessary, therefore, to draw distinctions that have a practical use rather than a philosophic basis; this point may be illustrated with a particular example.

It is well known that the antimony trichloride reaction with substances containing vitamin *A* can be refined by measuring not the colour itself produced with antimony trichloride, but the two spectral bands that give rise to the colour. This refinement of the "chemical" blue test is generally regarded as a spectroscopic test, that is to say, a physical one. The direct spectroscopic test for vitamin *A*, whereby, without the use of any chemical reagents other than solvents, we measure the intensity of an absorption band at $328m\mu$ invariably shown by products containing vitamin *A*, is clearly a non-chemical test, differing from the antimony trichloride test in that no reagents are used. In these notes neither it nor the spectroscopic modification of the antimony trichloride test will be described further, and this limitation is made for the purely practical reason that spectrographic or spectrophotometric technique is not available at present to many analysts.

Before summarising briefly our present knowledge of the chemical composition of the various vitamins it may be of use to make one or two general observations on the analytical procedure that must be adopted for their determination.

We have to deal here with the estimation, in the most favourable cases with the determination, of substances that may legitimately be described as "trace" substances, however fundamental their importance to human and animal health. From the point of view of the analyst, the estimation of a vitamin in a food, natural or reinforced, is a problem of the same nature as the estimation of some of those metals that have also been proved essential to life, though they are present at very low concentrations in most natural products. The determination of any main constituent of food—fat, protein, carbohydrate, mineral matter, and water—is carried out either without actually separating it completely from the other constituents, or after methods of separation that actually break down completely the other constituents. Reduction methods for determining sugars in complex solutions and the ordinary Kjeldahl nitrogen determination illustrate these procedures.

Such methods are inapplicable to the determination of trace substances. With rare exceptions it is not merely necessary to separate the trace substance wholly or partly from the main constituents, but it is necessary to do so by processes sufficiently mild to prevent the destruction of the substance being determined. The analyst's style is, in a sense, severely cramped in these circumstances, although the problems they present have led to some of the most beautiful of all analytical methods.

The determination even of such substances as the alkaloids, many of which give characteristic, if not completely specific, colour reactions, involves at least a partial separation from natural sources, though the alkaloidal content of plants is, in terms of weight, far higher than the content of vitamins, apart from a few exceptional cases. It is also a permissible generalisation to say that, the more we leave estimation and approach determination of trace substances, the more specific are the chemical reactions involved, and the more closely must we approach actual isolation of the substance to be evaluated.

It is, therefore, to be expected that our progress towards the successful chemical determination of vitamins in foods and other products, will go side by side with a general advance in methods for their isolation. In what follows, the vitamins will not be treated in alphabetical, that is, in chronological, order, but divided, according to the conventional classification, into water-soluble and fat-soluble. No reference will be made to the physiological properties that constitute the ultimate basis for their characterisation, but their composition, as far as it is known, is stated below, as well as their approximate concentration in certain sources. These facts are given partly for convenience of reference and partly to illustrate the general observations made above.

VITAMIN *B* (B_1, B_2, etc.).—The most probable formula for vitamin B_1 appears to be

$$C_{12}H_{20}O_2N_4S \quad \textit{or} \quad C_{12}H_{18}O_2N_4S.$$

It is certainly a basic substance, though not a primary amine, and it seems now to be generally agreed that sulphur is present in the molecule, and is split off when the vitamin is heated with alkali. The occurrence of a ring system is highly probable, but there is little more that can be said definitely about its chemical nature save that it is relatively labile to oxidation at p_H values above 7, and relatively stable in acid solution.

APPROXIMATE CONCENTRATION OF VITAMIN B_1 IN TYPICAL SOURCES

	Parts per 10^6
Dried yeast	16
Wheat germ	5
Fresh yeast	4

Recent work by Kuhn and his associates (*J. Soc. Chem. Ind.*, 1933, **52**, 981) indicates that vitamin B_2 is probably identical with a crystalline orange-brown fluorescent pigment, lactoflavine, that can be isolated from milk and whey (see Booher, *J. Biol. Chem.*, 1933, **102**, 39). Ovoflavine, present in egg-white, appears to be the same substance. The most probable formula is $C_{17}H_{20}O_6N_4$.

Four of the oxygen atoms are in hydroxyl groups that can be acetylated. Two of the nitrogen atoms are in the grouping -NH-CO-NH-, probably belonging to a ring system. The other nitrogen atoms seem to be tertiary and correlated with the conjugated double bonds that determine the colour.

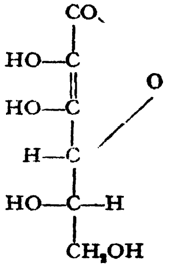
APPROXIMATE CONCENTRATION OF VITAMIN B_2 IN TYPICAL SOURCES

	Parts per 10^6
Liver or kidney	20–40
Yeast (fresh)	15
Muscle ..	2·5–5
Egg-white ..	1·5–3
Cow's milk	1·2–1·5

Of the remaining vitamins of the *B* group, B_3, B_4, B_5, and substance "*Y*" (Chick and Copping, *Biochem. J.*, 1930, **24**, 1764), practically nothing is known save the rather close association of vitamin B_4 with adenine; it is, however, doubtful whether the association is in any way chemical. All that has been shown is that separation of adenine and vitamin B_4 from natural sources is accomplished by the same method.

VITAMIN *C* can now be identified with a sugar acid known as ascorbic acid, and having the formula

ASCORBIC ACID (VITAMIN *C*)



3-keto-*l*-gulonolactone
$C_6H_8O_6$

Contrary to expectation, it is the first vitamin not merely to have assigned to it a definite molecular formula, but actually to be synthesised by purely chemical means (Ault, Baird, Carrington, Haworth, Herbert, Hirst, Percival, Smith, and Stacey, *J. Chem. Soc.*, 1933, 1419).

APPROXIMATE CONCENTRATION OF VITAMIN *C* (ASCORBIC ACID) IN TYPICAL SOURCES

	Parts per 10^6
Paprika (fresh)	2000
Lemon-juice and orange-juice	500 to 750
Potato (fresh)	150
Milk (best)	25

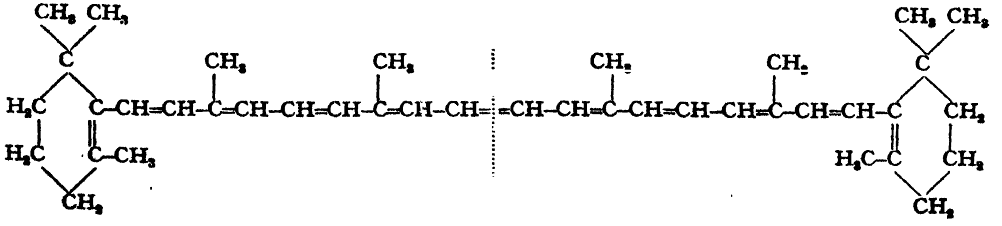
FAT-SOLUBLE VITAMINS.—Of the fat-soluble vitamins, under which heading for convenience we include carotene, vitamin *E* can be briefly dismissed, since little more can be said of its composition except that it appears to be closely related, as are so many substances of physiological activity, with the sterols.

APPROXIMATE CONCENTRATION OF VITAMIN *E* IN TYPICAL SOURCES

	Parts per 10^6
Evans's concentrate assumed ..	10^6
Wheat germ oil	< 2500
Wheat germ	< 250
Lettuce leaf	< 250

To *β*-carotene has been assigned the formula

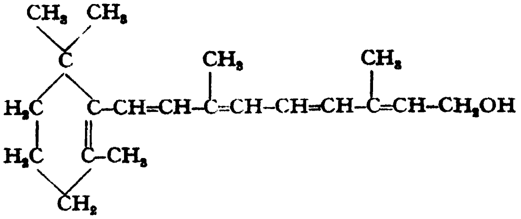
β-CAROTENE
$C_{40}H_{56}$



α-Carotene differs from this in that the positions of the double bonds are changed so that the molecule now has an asymmetric carbon atom. It is very likely that vitamin *A* is a partial oxidation product of half the carotene molecule, having the formula

VITAMIN *A*

$C_{20}H_{30}O$



The close association of carotene with vitamin *A* is inferred partly from the fact that the conversion of the latter into the former has been abundantly proved to take place in animals of several species, and is held to be so converted by the human organism, and partly from chemical work on degradation products of pure carotene and of highly purified concentrates of vitamin *A*. Both α- and β-carotenes have vitamin *A* activity, but the former only half that of the latter.

APPROXIMATE CONCENTRATION OF VITAMIN *A* IN TYPICAL SOURCES

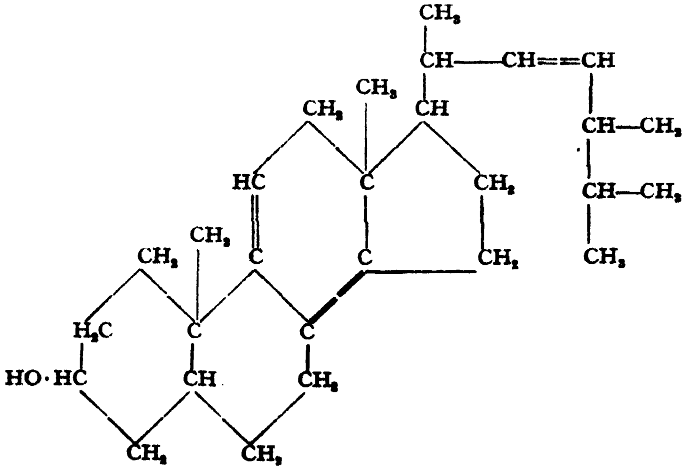
	Parts per 10^6
Various concentrates	2×10^5 to $9 \cdot 5 \times 10^5$
Halibut liver oil	10000 to 15000
Cod-liver oil ..	100 to 500
Butter-fat (best)	*5
Milk (best) ..	*0·2

* Assuming no activity due to carotene.

VITAMIN *D* is an isomer of ergosterol whose formula is

ERGOSTEROL (ANHYDROUS)

$C_{28}H_{44}O$



with the proviso that the position of the two double bonds in the ring system is not finally established. The nature of the isomeric change that takes place when ergosterol is converted to calciferol, to intermediate products and to photochemical degradation products is largely unknown. In certain respects calciferol differs from other sterols, particularly in the fact that it does not form an insoluble digitonide.

APPROXIMATE CONCENTRATION OF VITAMIN *D* (CALCIFEROL) IN TYPICAL SOURCES

	Parts per 10^6
Irradiated ergosterol..	2×10^5
C.L.O. concentrate (Zucker) ..	2500 to 5000
Cod-liver oil	2 to 8
Butter (best) ..	0·08
Milk	0·003

CHEMICAL REACTIONS.—We may now consider briefly the chemical reactions that have been used, or suggested, as bases for the estimation or determination of the vitamins. It is possible to pass very briefly over most of these, as they appear to have little practical value at the moment.

A suggested chemical test for vitamin B_1 in rice polishings and concentrates from that source has been described by Spruyt (*Mededeel. Dienst Volksgezondheid Nederland.-Indië*, 1930, **19**, 46; *C.A.*, 1930, **24**, 5802; *Chem. Weekblad*, 1930, **27**, 298; ANALYST, 1930, **55**, 460). After removal of possible interfering substances with norit and salicylic acid, the vitamin solution is treated with phosphotungstic acid, and the resultant precipitate reduced with zinc and hydrochloric acid, the intensity of the brown colour so produced being, it is claimed, a function of the vitamin B_1 content.

Apparently no work on this test has been carried out in this country, but it has been used by certain investigators in India (Acton, Ghosh and Dutt, *Ind. J. Med. Res.*, 1933, 103), who appear to find it to be of some value and to give results not inconsistent with biological assays. Attempts by us to apply it to active yeast extracts failed, partly, no doubt, because of the inadequacy of the description given in Spruyt's original paper.

There appear to have been no proposals for chemical tests for any other vitamins of the *B* complex; in view of our scanty knowledge of their chemistry, this is hardly surprising.

Vitamin *C* is a strongly reducing substance, and is therefore capable of being titrated with a number of oxidising reagents, such as iodine and certain dye-stuffs, notably 2.6-dichlorophenolindophenol. The iodine test is frequently used for estimating the degree of purity of samples of pure ascorbic acid, and is made the basis of routine control for the concentration of orange juice in certain Californian factories. Its main disadvantage is, of course, its lack of specificity; but it would seem to be useful, not only for such control purposes as the one mentioned, but also as a confirmatory test to that with the indophenol indicator. The last-mentioned was due originally to Tillmans, and has been rendered more specific by a modification due to Birch, Harris and Ray (*Biochem. J.*, 1933, **27**, 590). Though probably the most valuable test for vitamin *C* yet devised, it still leaves something to be desired in the way of specificity, partly because certain other substances undoubtedly behave like ascorbic acid (Birch, Harris and Ray, *loc. cit.*), when the test is carried out under the best conditions so far devised, and partly because some foodstuffs appear to contain substances that interfere with the reduction of the indicator (Svirbely, *Biochem. J.*, 1933, **27**, 960).*

The so-called Beszonoff test for vitamin *C* must also be mentioned, in passing, if only for historical reasons. This test was some years ago the subject of rather violent controversy, but there is little doubt that it is a not very specific test for phenolic substances; our present knowledge of the constitution of vitamin *C* makes it quite clear that its apparent validity in some circumstances can have been due only to coincidence (*cf.* ANALYST, 1921, **46**, 462).

For vitamin *E* there is, naturally, no chemical test whatever available.

For vitamin *D* no chemical test is available, except in the assay of one material, and one that is not, strictly speaking, a natural product. Since calciferol is produced by the method worked out at the National Institute for Medical Research, consisting in the treatment of ergosterol-free irradiated ergosterol with *m*-dinitrobenzoyl chloride, it should be possible to make use of this reaction for estimating the amount of vitamin *D* present in irradiated ergosterol. This can, in fact, be done, provided the irradiated material is sufficiently rich in calciferol, and provided a particle of the dinitrobenzoate is available, either in the hands of the analyst or in the air, for inoculation purposes. After complete removal of unchanged ergosterol from the irradiated material the methods recommended by the workers at the Institute can be followed almost exactly, and the separated dinitrobenzoate can be weighed, and its degree of purity quite accurately established by observation of its appearance and determinations of melting-point and optical rotation. We think that this procedure can legitimately be described as a genuine chemical assay, though it suffers from the considerable disadvantage that maximum separation of calciferyl dinitrobenzoate takes at best several days. Even so, there is almost always to be found by biological assay some residual antirachitic activity in the mother liquors. Nevertheless, it is satisfactory to be able to report that a number of biological assays, both by Dr. K. H. Coward at the Pharmaceutical Society's Laboratories and by ourselves, have shown very good agreement indeed with chemical assays carried out on the same material. For example, a recent assay on irradiated ergosterol gave the following results:

Biological assay:	
(Pharmaceutical Society):	14·5 × 10^6 units per grm.
(Glaxo Research Laboratory):	13·0 × 10^6 units per grm.
Chemical assay:	12·3 × 10^6 units per grm.*
(*Residual resin, probably contains calciferyl dinitrobenzoate equivalent to about	1 × 10^6 units per grm.)

Not only is this method difficult to apply to relatively low grade specimens of irradiated ergosterol, but so far it has been found entirely inapplicable to any natural source of vitamin *D*. Indeed, some recent experimental work has been interpreted to signify that there are in nature at least two other antirachitic substances differing from the synthetic calciferol. The work of Nussmeyer and

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* See also an important paper by Bessey and King (*J. Biol. Chem.*, 1933, **103**, 687; ANALYST, 1934, 122).

Massengale (*J. Biol. Chem.*, 1930, 87, 415, 423), of Steenbock, Kletzien and Halpin (*J. Biol. Chem.*, 1932, 97, 249), of De Vaney, Munsell and Titus (*Poultry Science*, 1933, 12, 215), of Bethke, Record and Kennard (*J. Nutrition*, 1933, 6, 413), of Ender (*Zeits. f. Vitaminforsch.*, 1933, 2, 241), and of Hess and Supplee (*Proc. Soc. Exp. Biol. Med.*, 1930, 27, 609) on the one hand, and the work at Reading on the other (Kon and Booth, *Biochem. J.*, 1933, 27, 1302), have been considered by some to indicate that the vitamin *D* in cod-liver oil and the vitamin *D* in butter-fat differ not only from each other but also from calciferol. At any rate, calciferol has never, so far, been identified in natural sources, though its antirachitic potency for human subjects has been definitely established by clinical observations (Spence, *Lancet*, 1933, Oct. 21st, 911).

There is no inherent reason why a substance with such definite properties as calciferol should not lend itself to chemical estimation. It is highly desirable that means for determining this substance should be worked out, for it is the least abundant vitamin in natural foodstuffs at the present day, and the one in which most people's diet is most likely to be deficient. It is also the only vitamin that has been added on any extensive scale to inactive foodstuffs, and means for establishing its presence and estimating its amount, other than biologically, are not unnaturally desired by Public Analysts and others.

BLUE TEST FOR VITAMIN *A*.—The so-called blue test for vitamin *A* will now be considered in rather more detail than the other tests so far surveyed. The reasons for this are two: first, of all the tests mentioned it is certainly the one that has been most extensively studied, and is most extensively used, both in biochemical research and in manufacturing routine; secondly, it is the one of which we, in our laboratories, have perhaps the most experience. We have indeed contributed something, we hope, to improving the technique of the test (Smith and Hazley, *Biochem. J.*, 1930, 24, 1942). A very useful bibliography of the literature on the subject was given recently in this journal (ANALYST, 1932, 57, 306).

It is hardly necessary to do more than mention, in passing, that the test is based upon the observation, made several years ago, that many cod-liver oils give a blue or purple colour with dehydrating agents like concentrated sulphuric acid. The most important step in advance of this was the discovery by Rosenheim and Drummond that, of all such reagents, arsenic trichloride gave the most intense and the least fleeting colour. A further modification, now well-known as the Carr-Price test, consisted in the replacement of arsenic trichloride by antimony trichloride, with a slight reduction in the sensitiveness of the test but a great increase in its usefulness.

Many papers have been published showing that the vitamin *A* content of cod-liver oil and other natural substances, biologically determined, is not simply correlated with the blue value of the oil determined by the Carr–Price technique. It is because of this that the Foreword to the 1932 British Pharmacopoeia is careful to disavow any intention that the limit colour test for cod-liver oil should be taken to indicate a limit for vitamin *A* content, or, indeed, to have any connection with it. Most workers in this field would now agree that the disclaimer in the Pharmacopoeia has to-day become over-cautious, consequent upon our increased knowledge.

We now know sufficient about this test to be able to make certain definite statements about it.

(i) In the vast majority of cases a high blue value indicates a high vitamin *A* content.

(ii) In the vast majority of cases a low blue value indicates a low vitamin *A* content.

(iii) The absence of blue value means the absence of more than a trace of vitamin *A*.

(iv) The intensity of blue given by a cod-liver oil is not in direct proportion to its concentration in the solutions used for the antimony trichloride test.

(v) The main reason why the colour intensity-concentration curve is not a straight line is the presence, in the saponifiable part of oils and fats, of substances inhibiting the production of the blue colour.

(vi) This fact explains why rich sources of vitamin *A* show a more nearly linear relationship of concentration and colour intensity than poor sources; a smaller weight of the substance is taken with rich than with poor sources, so that smaller amounts of the inhibiting substances are present in the test solution.

(vii) A preliminary concentration of the vitamin *A*-containing fraction of any natural product will increase the accuracy of the test, that is to say, will increase the closeness of its correlation with the content of vitamin *A*, biologically determined.

(viii) The most important method of concentration adopted for this purpose is the separation from the fatty constituents of the unsaponifiable matter, which should contain the whole of any vitamin *A* present if the process has been carried out with the necessary precautions.

(ix) There is some evidence from direct ultra-violet spectroscopy that a certain amount of vitamin *A* is lost even under the conditions laid down by Smith and Hazley (*loc. cit.*). The increased blue value obtained after saponification may well be the resultant of two separate effects, increased colour intensity due to removal of certain inhibitors and loss of vitamin during saponification. (See also Evers, and Crews and Cox, ANALYST, this issue, pp. 82, 85.)

(x) Vitamin *A* in fish liver oils is present mainly in an esterified form (Bacharach and Smith, *Quart. J. Pharm.*, 1928, **1**, 539), insoluble in ethyl alcohol; the vitamin itself is a primary alcohol, and is completely miscible with ethyl alcohol. It might be thought that the lack of linearity between concentration and colour intensity was a property of the ester as against the alcohol, but we have satisfied ourselves experimentally that this is not the case.

The importance of the different solubilities of the esterified and the unesterified forms of the vitamin lies in the fact that it is possible to extract an oil with alcohol without removing appreciable quantities of its vitamin *A*. Chevallier has shown that the ultra-violet absorption at $328m\mu$ is affected by the presence of free fatty acids (Chevallier and

Chabre, *Biochem. J.*, 1933, **27**, 298), so that it is necessary to carry out an extraction with ethyl alcohol on oils of high acidity before their spectroscopic examination. It has not been shown that such a procedure effects any improvement in the colour test, but the point may be worth investigating. It would, of course, be necessary to remove all traces of ethyl alcohol from an oil so treated, since alcohol is known to affect the stability of the blue colour produced with antimony trichloride. On the whole, separation of the unsaponifiable matter from oils has the advantage of removing free acid and most other interfering substances, and takes no more time than the direct test, if this has to be carried out in such a way as to enable a dilution curve to be prepared.

(xi) The reaction (that is the intensity and stability of the colour produced) is influenced by a number of factors, and the conditions for the test laid down in the 1932 Pharmacopoeia have been devised to standardise these factors as far as possible. Provided the Pharmacopoeial conditions are observed, the same observer using the same apparatus can obtain results of a considerable degree of reproducibility.

(xii) Spectroscopic examination of the two bands, whose combined effect is measured as a blue value on the tintometer, broadly substantiates the conclusions just stated, with an important exception.

(xiii) The relative intensities of the two bands have been found to differ for materials that apparently possess the same blue value. It has also been observed that the relative intensities of the two bands alter with increasing concentration of the vitamin *A* from a given natural source; in other words, that the increasing intensity of each band does not run *pari passu* with the increasing vitamin concentration as determined biologically and by direct spectrophotometry on the material.

(xiv) Certain substances, such as indole and skatole and their derivatives, have the property of greatly diminishing the intensity of one band ($617 m\mu$) with only slight effect on the other ($583 m\mu$).

(xv) Several of the limitations of the test are, in fact, inherent in the use of the tintometer rather than in the application of the reaction as such. Thus it has been shown by many workers that other substances produce blue or similar colours with antimony trichloride (*cf.* Levine and Richman, *J. Biol. Chem.*, 1933, **101**, 373); the reaction appears to be associated with the presence of conjugated double bonds. Very few of the colours produced, however, are likely to be mistaken for that due to vitamin *A*, since most of them differ either in shade or in stability. In no case has spectroscopic examination of the colours, where it has been carried out, revealed bands at 617 and $583 m\mu$, except with known sources of vitamin *A*. It is, therefore, the tintometric as against the spectroscopic modification of the test that limits its specificity in this respect.

(xvi) A factor limiting the usefulness of the colour test is that, for purely physiological reasons, the tintometer, used almost exclusively for measuring blue values, has a rather limited range of accuracy. Below 4 and above 10 we have found it hardly possible, and below 2 and above 14 quite impossible, to obtain consistent readings, even on the same solution, owing to matching difficulties; this makes the colour-concentration curves liable to considerable error at low and high concentration values. It is, therefore, necessary, when applying the test to oils and concentrates appreciably richer in vitamin *A* than low-grade cod-liver oils, to modify the B.P. technique, if it is to give quantitative results, and not merely to be used in a limit test, for which it was devised.

(xvii) The blue glasses used in the tintometer transmit light that is spectrally different from that transmitted by the blue colour produced in the test. It is probably for this reason that different observers often do not match the same solution with absolutely identical glasses. There are indications that, where personal variations occur, they are constant and additive. Mr. R. T. M. Haines, of the Crookes Laboratories, tells us that he can reproduce the values of other observers that normally differ from his, provided he knows what they call a "match"; it becomes simply a question of adding or subtracting a fairly constant figure from his own match. This point would also repay further investigation.

If the difference in reading between observers is caused by their different sensitivity to the two spectral bands produced, it is justifiable to say that again the tintometer rather than the reaction limits the utility of the test.

(xviii) A further point of difficulty arises in the use of the neutral glasses supplied in the tintometer for dulling colours that are too bright to be matched. Every neutral glass in the tintometer sets consists of superimposed red, blue and yellow glasses, each standardised to contain the same number of units of colour. There has been some controversy on the advisability and legitimacy of deducting the amount of blue in the neutral glasses used from the total blue colour shown by a solution on matching. Two quite different levels of vitamin *A* may be attributed by different observers to a very bright solution, according to whether the blue share of the neutral glass is or is not deducted from the total blue units. The standard practice at present seems to be against deducting the blue value of the neutral glasses, but we are still unconvinced of the logic of this practice. A recent paper by Morgan (*Biochem. J.*, 1932, **26**, 377) describes a modified technique of computing vitamin *A* potency from the values of the blue and yellow glasses used in the match, and was itself criticised in a note by one of us (Smith, *J. Soc. Chem. Ind.*, 1932, **51**, 1042). The matter should be regarded as still *sub judice*. The difficulty, of course, does not arise if the blue colour is estimated spectroscopically.

We have attempted above to set out as completely as possible all the salient facts about the nature of the reaction of vitamin *A* with antimony trichloride and the technique used in measuring "blue values." There is, further, some indication that certain oils have rather anomalous physical and chromogenic properties, and it would seem at present undesirable in important cases to rely solely upon physical and chemical criteria, if it is a question of comparing one oil or concentrate with another. Such anomalous behaviour as has so far been reported or experienced by ourselves is invariably in the direction of diminishing the apparent vitamin *A* content of an oil as determined by the colour test, whether on the oil itself or on its unsaponifiable matter. Exhibitors of the blue colour, as distinct from inhibitors, do not appear to be of importance, except in so far as other substances giving a blue colour may be present in a source of vitamin *A*. Even carotene, which, perhaps, of all substances most nearly simulates the behaviour of vitamin *A* when treated with antimony trichloride, can be distinguished from it spectroscopically; the absorption bands produced by carotene and antimony trichloride are different from those produced by vitamin *A* and antimony trichloride; further, the blue colour produced with carotene is relatively permanent.

The difference in physical and chemical properties between carotene and vitamin *A* has considerable analytical value, for it enables a distinction of importance from the point of view of dietetics to be drawn between the two sources of vitamin *A* activity in a substance like milk-fat, where both are present in amounts of the same order. Several different procedures have been recommended, and have in general led to similar results, as a means of discriminating between the two substances. The carotene can be estimated directly by means of the absorption coefficient of its characteristic bands in the visible spectrum; the total "apparent" vitamin *A* content can be estimated either biologically, or by means of the antimony trichloride test, and the amount of "apparent" vitamin *A* actually due to carotene deducted from the result of biological or physico-chemical test. Alternatively, the carotene can be removed by adsorption, and the amount of vitamin *A* determined by estimation of the band at $328m\mu$, which cannot be done in the presence of carotene, as this possesses an overlapping band in this region of the ultra-violet. Methods of this kind have been adopted by Gillam, Heilbron, Morton, Bishop and Drummond (*Biochem. J.*, 1933, **27**, 878), by Baumann and Steenbock (*J. Biol. Chem.*, 1933, **101**, 547), and by Booth, Kon, Dann and Moore (*Biochem. J.*, 1933, **27**, 1189).

It will be clear that there are still many pitfalls awaiting the unwary user of the antimony trichloride colour test. Nevertheless, it can be truly said that it is difficult to exaggerate its importance and value, especially to all those who have applied the test to the preparation and standardisation of vitamin *A* concentrates; they will surely agree that without it difficulties of manufacture and control would have been enormously increased, and this could only finally express itself in an increased price to the public of standardised vitamin *A* preparations. It is possible now to use the blue test, suitably adapted, as a routine process in the control of factory operations and to have recourse to the spectrophotometer and the rat for final and more specific confirmation of results obtained with the blue test. A similar procedure is now possible, in certain circumstances, in the large-scale concentration of vitamin *C*, but we are not yet in so fortunate a position in the manufacture and control of any other vitamin.

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Notes on the Determination of Vitamin *A*

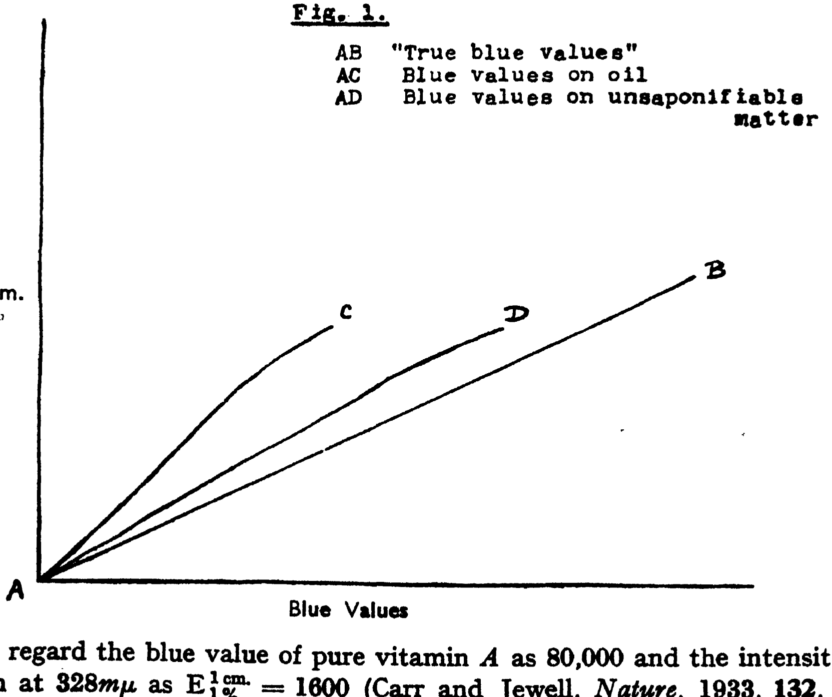
BY NORMAN EVERS, B.Sc., F.I.C.

I. COD-LIVER OIL. THE RELATIONSHIP BETWEEN THE "BLUE VALUE" OBTAINED ON THE ORIGINAL OIL, THE "BLUE VALUE" OBTAINED ON THE UNSAPONIFIABLE MATTER AND THE "TRUE BLUE VALUE" OF COD-LIVER OIL

WITH reference to the technique of the antimony trichloride colour test, it seems desirable to emphasise the necessity of adjusting the concentration of the oil solution so that the final reading in the tintometer is taken at 5 blue units. Serious differences may be caused by taking readings even at 4 or 6 blue units.

Dyer (ANALYST, 1933, **58**, 709) has reported on a series of 39 samples of cod-liver oil on which he determined the blue values of the original oils and of the unsaponifiable matter extracted by the method of Smith and Hazley (ANALYST, 1931, **56**, 265). At the same time Wilfred Smith and the author (*Quart. J. Pharm.*, 1933, **6**, 329) published a graph for a series of cod-liver oils showing the relationship of the blue values determined on the original oils and the intensity of absorption at $328m\mu$.

Fig. 1.



If we regard the blue value of pure vitamin *A* as 80,000 and the intensity of absorption at $328m\mu$ as $E^{1\,cm.}_{1\%} = 1600$ (Carr and Jewell, *Nature*, 1933, **132**, 92), we can express this as a linear relationship graphically by the line AB in Fig. 1. Assuming that the value of $E^{1\,cm.}_{1\%}$ at $328m\mu$ is a quantitative measure of vitamin *A*, it is possible to calculate by means of this graph the "true blue value" of an oil from the value of $E^{1\,cm.}_{1\%}$ $328m\mu$.

These values have been calculated for a series of 48 samples of cod-liver oil. The results are expressed in the following table:

TABLE I

Oil	$E^{1\,\text{cm.}}_{1\%}$ $328m\mu$	Blue value on original oil (x)	"True blue value" (y)	Ratio $y : x$
1	0·31	7·2	15·2	2·111
2	0·40	7·4	19·6	2·649
3	0·43	8·6	21·0	2·442
4	0·42	9·0	20·2	2·244
5	0·59	4·4	28·3	2·482
6	0·53	12·7	25·7	2·024
7	0·84	13·2	40·6	3·076
8	0·71	13·4	34·0	2·537
9	0·73	13·4	35·2	2·627
10	0·77	13·6	37·4	2·750
11	0·75	14·0	36·0	2·571
12	0·67	14·4	32·4	2·250
13	0·75	14·4	36·4	2·528
14	0·67	14·7	32·4	2·204
15	0·71	15·1	34·4	2·278
16	0·82	16·0	39·4	2·463
17	0·93	16·0	45·2	2·825
18	0·67	16·1	32·4	2·012
19	0·91	16·8	44·0	2·620
20	0·63	17·0	30·5	1·794
21	0·71	19·0	34·6	1·821
22	0·89	19·4	43·0	2·216
23	0·93	21·5	45·3	2·107
24	0·77	21·5	37·0	1·721
25	0·83	22·0	40·2	1·827
26	1·37	22·8	67·4	2·956
27	1·08	23·0	52·4	2·278
28	0·91	24·0	44·1	1·837
29	1·06	24·0	52·0	2·167
30	1·11	24·0	54·2	2·258
31	1·17	24·0	57·4	2·392
32	1·17	25·0	57·6	2·304
33	1·05	26·5	51·4	1·940
34	1·28	26·5	63·0	2·377
35	1·16	27·2	56·8	2·088
36	1·38	27·5	68·2	2·480
37	1·17	28·0	57·0	2·036
38	1·05	28·2	51·4	1·823
39	1·17	28·6	57·4	2·007
40	1·22	29·0	59·6	2·055
41	1·25	31·5	61·6	1·956
42	1·55	31·6	77·2	2·439
43	1·29	32·0	63·4	1·981
44	1·18	33·0	58·0	1·758
45	1·42	37·8	71·0	1·875
46	1·53	44·0	76·2	1·732
47	1·31	48·0	64·6	1·345
48	1·37	48·0	68·0	1·417

The mean value of log y—log x for this series was found to be 0·33645 or log 2·17. Hence, on the average, the "true blue value" of the oil is 217 per cent. of the blue value determined on the oil itself. Applying the same method, Dyer (*loc. cit.*) found that for his 39 oils the blue value of the oil when determined on the unsaponifiable matter was on the average 161·5 per cent. of the blue value determined on the oil itself. Hence it appears that the blue value determined on the unsaponifiable matter is intermediate between the blue value determined on the oil itself and the "true blue value." From this it may be concluded that Smith and Hazley's method does not remove the whole of the material which is responsible for the reduction of the antimony trichloride colour.

Another point which emerges from these results is that there is a tendency for the ratio $y : x$ to become less for oils of high blue value, *i.e.* these values more nearly approach "true blue values." This is to be expected, since oils of very high blue value such as halibut liver oils lie on or near the line AB in the graph. Dyer (*loc. cit.*) found that the ratio of the blue value determined on the unsaponifiable matter to the value determined on the oil was on an average the same for oils of high and low blue value. Hence blue values determined on the unsaponifiable matter also approach nearer to "true blue values" for oils of high blue value.

II. A PLEA FOR GREATER UNIFORMITY IN EXPRESSING RESULTS FOR VITAMIN *A*.

Of the numerous methods of expressing results for vitamin *A*, the following list includes the more important, but cannot be said to be exhaustive:

(*a*) *Biological Units.*—(i) The *carotene unit,* which has been officially adopted as the international unit of vitamin *A*. Owing to difficulties in obtaining uniform results with carotene, this standard has not yet come into practical use.

(ii) The *U.S.P. Biological Unit.*—These units are usually meant when "biological units" are mentioned.

(*b*) *Units based on Chemical or Physical Tests.*—(i) The "blue value" determined on the oil itself (B.P. method).

(ii) The "blue value" determined by the method of Drummond and Hilditch (*Empire Marketing Board Report,* ANALYST, 1931, **56**, 533), which gives values about one-half of those given by (i).

(iii) The "blue value" determined on the unsaponifiable matter.

(iv) The number of "blue units" per mgrm. of oil.

(v) The intensity of absorption at $328m\mu$ expressed as $E^{1\,\text{cm.}}_{1\%}$.

(vi) The percentage of vitamin *A* calculated from $E^{1\,\text{cm.}}_{1\%}$ at $328m\mu$, regarding this value for pure vitamin *A* as 1600.

In addition to these, there is a method much to be deprecated, *viz.* the multiplication of the blue value by an arbitrary factor to give "biological units." I have even encountered an extension of this method in the use of a second factor to convert the "blue value" into units of vitamin *D*!

It is easy to imagine the confusion of the buyer of cod-liver oil when he is faced with this variety of expressions. Needless to say, there is a tendency for the seller to use the system of units which gives the most impressive figure.

Having regard to the simplicity and rapidity of the physical or chemical tests, and to the fact that they are at least equal to the biological test in accuracy, it seems desirable that, at any rate for commercial purposes, one of these methods should be generally adopted. The spectrographic method has the disadvantage of requiring a special apparatus, which, even at the greatly reduced cost of the simplified form exhibited by Professor Drummond, is still a serious item of expenditure.

The "blue value" when determined on the unsaponifiable matter has been shown by Coward, Dyer and Morton (*Biochem. J.*, 1932, 26, 1593; ANALYST, 1932, 57, 368) to give values which agree better with the biological values than the "blue value" determined on the original oil.

In spite of this, it appears doubtful whether the trouble of preparing the unsaponifiable matter is really worth while. The graph in the paper by the author and Wilfred Smith (*Quart. J. Pharm.*, 1933, 6, 329) shows that the blue value determined on the oil does give an approximate idea of the vitamin *A* content of the oil, and one that is sufficiently accurate for most commercial purposes. Further, there is the fact that it is based on the method described in the British Pharmacopoeia.

Taking all things into consideration, there seems to be little reason with ordinary commercial oils to go beyond the blue value determined on the oil itself by the B.P. test suitably adapted, except in special cases where greater accuracy is desirable.

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The Relationship between the Carr-Price Value and the 328$m\mu$ Absorption Coefficient of Preparations containing Vitamin *A*

BY SYDNEY K. CREWS, A.I.C., AND STANLEY J. COX

SINCE 1926 it has been the practice in these laboratories to examine all products containing vitamin *A* for their chromogen-content by the Carr–Price antimony trichloride reaction,[1] and during this period many hundreds of determinations have been made annually. The information thus afforded has proved a valuable aid in making progress which would have been impossible in so short a space of time had the biological method of feeding tests been the sole means of evaluation.

Much work has been published recently in this country by Heilbron, Morton, Gillam and others[2,3,4] dealing with the selective absorption shown in the ultra-violet region of the spectrum by products containing vitamin *A*, and also with the differentiation of chromogenic substances by the spectroscopic examination of the blue colour produced by the antimony trichloride reagent.[5] Good evidence has been adduced to show that vitamin *A* activity is due to only one of these chromogens, namely that with an absorption of 328$m\mu$ in the ultra-violet. We have, therefore, examined our vitamin *A* products by spectrophotometry as well as by determination of chromogen content by the Carr–Price method.

The antimony trichloride test for cod-liver oil adopted in the B.P. 1932 is essentially the Carr–Price test. The quantity of oil taken for the B.P. test is

0·04 grm.; the original test was on 0·04 c.c. The antimony trichloride reagent is a saturated solution of antimony trichloride in dry alcohol-free chloroform; the original reagent was a saturated solution in B.P. chloroform containing a small amount of absolute alcohol. The colour produced on addition of the reagent to the chloroformic solution of the oil is matched in a glass cell having a square cross-section of 1 cm. side; in the original test a tube or cell of 8 mm. across was used.

For some considerable time before the publication of the B.P. 1932, we, in conjunction with other workers in this line, had been using the square-sectioned cell of 1 cm. side, and also had used dry alcohol-free chloroform for preparing the reagent. Throughout all our experiments, we have used the Lovibond Tintometer for measuring the intensity of the blue colour produced in the reaction. We have always matched the colour at the point of maximum intensity, and used red or yellow glasses, or both, where necessary, in addition to blue glasses, in order to obtain an exact colour match.

The details of the Carr–Price test are now fairly well known, but one or two points in the actual working may be of interest. It has been found that the best results are obtained when the actual tintometer readings are between 4·0 and 6·0 of blue, the observation being made at the moment of maximum colour intensity and not at the end of any time period. Either daylight or artificial daylight may be used, but if the latter, then a difference of 0·1 blue must be distinctly visible. The Tintometer Company make an attachment for their instrument which we find very suitable. The use of a specially designed automatic pipette for the antimony trichloride reagent is a great advantage, as this solution is rather corrosive, besides being hygroscopic. Another point is that one should not look down the eyepiece of the tube of the tintometer when the reagent is being poured into the cell, or the deeper blue produced by the first few drops of the reagent will make the final match more difficult.

The use of each eye alternately is an advantage, as ocular fatigue is thus minimised. In the final match about three seconds is the maximum time to look at the colours; after this the eye becomes less sensitive and good matching is impossible.

When these conditions are observed, there is no difficulty in obtaining concordant results by various workers, even in different laboratories.

The B.P. 1932 test is only a limit test to prevent the use of cod-liver oils containing less than a minimum of chromogenic substances, and the conditions laid down for the test are well defined. The test as described in the Pharmacopoeia, however, is not suitable for the evaluation of oils of higher chromogen-content or for vitamin *A* concentrates. For these, the concentration of the chloroform solution of the oil should be such that 0·2 ml. mixed with 2 ml. of the reagent produces a colour lying between 4·0 and 6·0 Lovibond blue. The result is then calculated to the proportionate colour for 0·04 grm. Owing to the curve of colour production, the colour calculated in this way will be quite different from the actual colour produced by 0·04 grm. in the quantities of chloroform and reagent used in the test.

While a comparison of the blue value with the results of spectro-photometric and biological tests shows considerable variation with cod-liver oils, this does not apply to purified preparations of vitamin *A*. Remarkable changes occur in many oils on keeping. A very freshly prepared oil may have at first a negligible blue value which then rises, at first quickly, then more gradually, to a peak value, and, finally, with age, generally falls again. Both the rise and the fall may be accelerated by certain oxidising agents.

A determination made on the unsaponifiable fraction of a liver oil by the Smith and Hazley method (*Biochem. J.*, 1930, **24**, 1942; ANALYST, 1931, **56**, 265) usually gives a higher figure than one made directly, and affords a truer indication of the vitamin *A* content. We have occasionally examined oils which give even as much as three times the blue value by this method as by a direct determination on the original oil, and, judging by our spectrographic work on concentrates, we are inclined to think that even after hydrolysis the vitamin-content indicated by the antimony trichloride method may still be too low. For example, one of the oils recorded gave a Carr-Price value of 10·0, which increased to 30·0 on the unsaponifiable fraction, yet the E figure showed a value of 1·0, which in a purer concentrate would correspond with a blue value of about 50·0. There are, therefore, inhibiting substances present in the oil which cause the low blue value, and these substances are, in a large measure, removed by hydrolysis.

Although other chromogenic substances which give a blue colour by the Carr–Price test are often present in cod-liver oils, we have never found an oil of which the blue value is above what may be expected from the absorption at $328m\mu$. The explanation appears to be that the inhibiting substances present cause a greater depression of the blue colour than any increase due to chromogenic substances other than vitamin *A*. It follows that the figures given by the Carr–Price method indicate the minimum content of vitamin *A*.

The absorption at $328m\mu$ in the ultra-violet corresponds with that given at 572–$584m\mu$ by the blue compound resulting in the antimony trichloride reaction. The absorption at $328m\mu$ can be determined with greater accuracy than that at 572 to $584m\mu$, owing to the instability of the antimony trichloride blue substance, and has the additional advantage of more readily providing a permanent photographic record. In the present paper this value has been correlated with the blue value of many vitamin *A* products derived from various sources—fish-liver oils, mammalian-liver oils, concentrates, etc. It was pointed out by Morton that the spectrographic absorption in concentrates is less than would be expected from colorimetric determinations of the blue value, as compared with cod-liver oil, and our results obtained during the routine examination of a large number of samples confirm this, as will be seen from the tabulated results on p. 89.

APPARATUS.—The apparatus employed consists of the latest type of Bellingham and Stanley ultra-violet quartz spectrograph fitted with a B. and S. short-focus rotating sector photometer mounted directly on the instrument.

Illumination is effected by a condensed spark between tungsten steel electrodes 4 mm. apart. A voltage of 10,000 was obtained from 105 volt A.C. mains by the use of suitable transformers and a condenser. The current for driving the motor rotating the sector photometer was also taken directly from the mains by the use of suitable resistances.

The spectrograms were recorded on either plates or flat cut films (10×4 in.) with H. and D. speed of about 700. We have found either Imperial Eclipse plates or Barnet portrait films to be particularly suitable.

The determination is made by taking a series of pairs of photographs of the spectrum, each pair consisting of one spectrogram taken through a solution of the substance and another taken through the same thickness of the solvent. By means of a sector photometer consisting of two rotating shutters, one of which is adjustable for the size of opening, the time of exposure of the individual halves of each pair of spectrograms is varied so that the relative exposures through the solvent are decreased quantitatively. In this way points can be found on each pair of photographs where the density of the two halves is the same, showing that at these points the intensities of the two beams of light, multiplied by the relative exposures, are equal. As the ratio of the exposures decreases, the points of equal density of the spectrograms become closer together, until at the head of the band they become coincident. This point is used for the calculation of the "extinction coefficient," E, which is the logarithm of the ratio of the intensity of the transmitted light to the incident light.

After a series of exposures has been made through a number of pre-determined openings of the sector, the development, fixation and drying are carried out in the usual way. The negatives are inspected on a suitably illuminated viewing box, and the "cross over" points are marked, and from these the "extinction coefficients" are calculated.

In the case of vitamin *A* preparations, it is usual to calculate to a 1 per cent. concentration and a 1-cm. cell, and to specify the particular wave-length or band at which absorption has taken place. This is usually expressed as $E^{1\,\text{cm.}}_{1\%}\ 328m\mu$.

The solutions used were adjusted to concentrations such that readings of approximately between 0·8 and 1·2 were obtained for a 1-cm. quartz cell.

A small correction for the absorption due to substances other than vitamin *A* may be made if required, but in the Table given on p. 89 this has been omitted, as its value is very small.

The solvents used for these experiments were absolute alcohol and cyclohexane, which had been specially purified for spectrographic work, and showed no appreciable U.V. absorption above 220$m\mu$. The concentrations varied from 1·0 per cent. with oils to 0·0006 per cent. with vitamin *A* preparations of high potency.

Carotene and Vitamin *A*.—Spectrophotometry has confirmed the results recorded by others who have shown that the ultra-violet absorption of Vitamin *A* is not due to carotene or to similar colouring matters. A spectrogram of a sample of pure carotene B.D.H. shows that absorption occurs in a totally different part of the spectrum from that given by vitamin *A*, namely, at about 450$m\mu$, which is in the visible region, and that the absorption in the ultra-violet region is negligible.

A comparison of the curve with those obtained for products containing vitamin *A* shows that in all cases the peak of the curve for vitamin *A* apparently lies between 325 and 330$m\mu$, although it may be rather flat.

Vitamin *D*.—The curves obtained for vitamin D ("calciferol," with a potency between 40,000 and 45,000 units per mgrm.) have their peak at 265 to 270$m\mu$.

Product	Blue value	Blue value on unsap. fraction	$E^{1\,\text{cm.}}_{1\%}$ 328 $m\mu$.	$\frac{\text{B.V.}}{\text{E}}$	$\frac{\text{B.V. unsap.}}{E^{1\,\text{cm.}}_{1\%}\ 328\,m\mu.}$
"Cattle" oil	0·6		0·3	2	
Cod-liver ,,	1·6		0·35	4·57	
,, ,,	7·6	12·0	0·4	19	30
Medicinal cod-liver oil	7·2	15·0	0·65	11	23·07
,, ,, ,,	11·2		0·7	16	
	12·0		0·75	16	
	10·8		0·8	13·5	
	8·8	18·8	0·8	11	23·5
	8·0		0·8	10	
	9·2	32·0	0·85	10·8	37·65
	12·0		0·9	13	
	20·0		0·9	22	
	20·0		0·95	21	
	17·6	20·0	1·0	17·6	20
	10·0	30·0	1·0	10	30
	13·2		1·1	12	
	22·0	30·0	1·1	20	27·3
	28·0		1·2	23	
	28·0	40·0	1·2	23·3	33·3
	13·2	22·5	1·2	11	18·9
	20·0		1·4	14·2	
	28·0		1·4	20	
,, ,,	32·0	46·0	1·6	20	28·75
Med. cod-liver oil	20·0		1·7	12	
,, ,, ,,	32·8		1·7	19	
Dog-fish liver oil	60·0		1·9	32	
Coml. fish-liver oil	66·0		2·4	27·5	
	110		3·3	33	
	200		5·5	36	
,, ,, ,,	197		6·0	33	
,, ,, ,,	570		10·8	53	
Vitamin *A* concentrate	530		8·0	66·25	
,, ,,	550		12·0	45·8	
,, ,,	720		16·0	45	
,, ,,	900		18·0	50	
,, ,,	1000		20·0	50	
,, ,,	1400		28·0	50	
,, ,,	2000		44 0	45·45	
,, ,,	2900		60·0	48·3	
,, ,,	3000		45·0	66·7	
,, ,,	4800		100	48	
,, ,,	5760		94	61	
,, ,,	7000		146	48	
,, ,,	10000		180	55	
	1050		28·0	39	
	1400		28	50	
	2000		44	44	
	3000		37·5	80	
	3000		45	66·7	
	4800		100	48	
	5760		94	61	
	7000		146	50	
	7000		141	50	
	10000		180	55	
	11000		225	50	
	22000		480	46	
	27000		550	49	
	40000		800	50	
	50000		1100	49	
	57000		1160	49	
	63000		1128	55	
	76000		1360	56	
	76000		1440	52·8	
	80000		1600	50	

TABLE II

VITAMIN *A* CONCENTRATES

Mean ratio of blue components of colour to yellow and brightness

Strength of concentrate	Number of samples	Blue	Yellow	Brightness
100–500	16	1	0·305	0·10
500–1000	27	1	0·32	0·12
1000–2000	14	1	0·33	0·13
2000–10000	9	1	0·34	0·16
10000–50000	26	1	0·34	0·17
50000–80000	39	1	0·35	0·19

CONCENTRATES.—As will be seen from Table I, the B.V./E ratio becomes much more constant as the B.V. increases. An interesting point which has emerged from the determination of the chromogenic contents of concentrates is the difference in the colour analysis of the blue compound after the addition of the antimony trichloride. With oils, a pure blue or violet blue is possible, but with concentrates the colour is a bright greenish-blue.

Table II gives the colour analysis for the colour produced with various concentrates with Carr–Price values ranging from 100 to 80,000, from which it will be seen that for the highest concentrate examined the colour produced was of the order 1·0 blue + 0·35 yellow+0·19 brightness.

From a consideration of the ratio B.V./E it will be seen that:

(*a*) With cod-liver oils of blue value up to 20 the figure usually lies between 12 and 20, but when the value is determined on the unsaponifiable fraction the figure shows a marked increase, and is about 30.

(*b*) With cod-liver oils of blue value up to 60 the values approach 30.

(*c*) With high value commercial fish liver oils up to 600 the figure is in the neighbourhood of 50.

(*d*) Concentrates gave a value of approximately 50.

The authors wish to thank Dr. F. H. Carr for his help and advice throughout this work, and the Directors of The British Drug Houses, Ltd., for permission to publish this note.

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The Titration of Vitamin *C* in Citrus Juices

BY A. H. BENNETT, B.Sc.

(*Read at the Meeting November 1st*, 1933)

THE citrus fruits differ from most others in the fact that their valuable dietetic qualities are contained almost entirely in the juice; and since this juice is readily expressed and can be preserved for long periods in a palatable state, a large part of the public consumption is in this form. Of these qualities, the anti-scorbutic power is among the most important, and it is of interest, therefore, to ascertain the extent of natural variation of this power, and the degree in which it remains undiminished in the preserved juice, and to determine the conditions most favourable to its conservation.

For this purpose a titration method which can show the state of the juice from day to day is evidently the most convenient, and the method of Tillmans—titration with a solution of 2·6-dichlorophenol-indophenol—has been applied to the examination of a considerable number of samples of Sicilian lemon and orange juices, both freshly-prepared from the fruit and preserved by the usual commercial methods.

The process used and the results obtained are described elsewhere (*Biochem. Journal*, 1933, **27**, 1294; ANALYST, 1934, 52), but it may be added that since that paper was submitted for publication the modified method of standardising the indicator solution, proposed by Tillmans, Hirsch and Vaubel (1933), has been employed.

Twenty-five ml. of the indicator solution (approximately $N/1000$) are titrated in presence of 5 ml. of saturated sodium oxalate solution, with a $N/500$ solution of ferrous ammonium sulphate containing $N/250$ sulphuric acid, until no colour remains.

The results agree with those obtained by the use of titanous chloride, and the process is more convenient, owing to the extreme instability of the titanous chloride solution.

The juices examined, whether extracted in the laboratory or in the factory, did not contain enough iron to affect the titrations, but it is, of course, possible that some commercial samples might contain appreciable quantities of ferrous iron, and this should be borne in mind. The iron present can be determined colorimetrically and a correction applied.

The indicator solution is itself unstable, even in the buffered solution described. If it is kept for more than a few days some change takes place which causes a red-violet tint during the titration, and makes the end-point obscure.

NATURAL VARIATION.—In earlier work on vitamin *C* by the biological method it was generally assumed that the antiscorbutic potency of freshly prepared lemon or orange juice was constant, and, in fact, the international unit is defined as being the value of 0·1 ml. of lemon juice.

Since crystallised ascorbic acid has been available for experiment, doubt has been cast on this assumption. Key and Morgan (*Biochem. J.*, 1933, **27**, 1030), in a series of experiments comparing the effects of different doses of ascorbic acid and of lemon juice, found considerable variation in the relations between the two, and their value for ascorbic acid was about half that found by Szent-Györgyi. They consider it probable that the variation was in the lemon juice used as a standard.

Nelson and Mottern (*Ind. Eng. Chem.*, 1933, **25**, 216) found that in the series of experiments there described, 1·5 ml. of the orange juice employed had given a much lower degree of protection than had been obtained in some earlier trials. These experimenters give the results of the titration of their juice with dichlorophenol-indophenol, and their figures (6·6 to 7·1 ml. of *N*/1000 indicator solution to 1 ml. of juice) are considerably lower than those found for Sicilian orange juice of the season 1932–33 (10·3 to 11·8), and appreciably below the average for lemon juice of the same period.

Conn and Johnson (*Ind. Eng. Chem.*, 1933, **25**, 218) make similar observations on the apparent variability of antiscorbutic potency.

These biological observations are, therefore, in agreement with the results of titration, which, as reported in the above-mentioned paper, show that the highest results obtained are double the lowest, and that, even excluding extremes, a variation of 25 per cent. is common.

The laboratory-pressed juice was usually made from lemons within a few hours of picking. There were some indications that the titration value of the juice was higher when the lemons were stored for some weeks before squeezing. This, however, requires confirmation with much larger numbers of fruit before any conclusions can be drawn.

PRESERVATION IN THE JUICE.—The results obtained with juices preserved in any of the usual ways showed that the effective prevention of fermentation in the juice was accompanied in all cases by a continual diminution of reducing power, ending in its total disappearance after a few weeks. These experiments were made with comparatively small volumes of juice kept at the laboratory temperature; and, since there is reason to think that the effect depends on the inhibition of a protective agency followed by atmospheric oxidation, it is probable that the rate of loss will vary considerably in different circumstances, and may very likely be lower when large volumes of juice are stored.

It was indicated in our earlier paper that, when air is excluded, the life of the reducing factor in sterilised juice is considerably prolonged. These experiments have been continued.

Lemon juice, filtered with the aid of asbestos and kieselguhr, was placed in a series of Thunberg tubes and pasteurised for an hour at 65° C. The air was exhausted by a pump and the tubes were closed.

The original titration value of the filtered juice was 6·9 ml. of indicator solution per 1 ml. of juice.

The tubes were opened at intervals, and, after 35 days, the value was 5·1 ml., whereas juice pasteurised and left exposed to air (in a tube with a stopper of cotton-wool) lost its reducing power completely in 12 days.

A similar experiment was made in which the juice, instead of being pasteurised, was treated with sulphur dioxide (0·3 grm. per litre). The original value of 7·3 was reduced to 5·0 after 56 days, and to 4·3 after 110 days, whilst, when there was access of air, the reducing power was completely lost in 26 days.

It seems, therefore, that the exclusion of air greatly retards, but does not altogether prevent, the disappearance of the reducing factor in sterilised or preserved juices when kept at room temperature. No experiments have yet been made on the effect of cold storage, which, from the biological point of view, has been investigated by several American workers.

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DISCUSSION ON THE CHEMICAL TESTS FOR VITAMINS

DR. LESLIE J. HARRIS said that he would like first to make two points with regard to the antimony trichloride test for vitamin *A*: (1) For an accurate quantitative estimation of the vitamin *A* content of a foodstuff by this method it was essential to saponify first, and make the test on the unsaponifiable residue. Various interfering substances were found in varying amounts in different materials, and caused seriously misleading results unless this precaution was taken to get rid of their effect. Thus the B.P. test for cod-liver oil was not an accurate quantitative method at all, but only a qualitative, or "limit" test; it enabled one to say if a given specimen was "up to scratch" or not, but one could not certify accurately from it the exact quantitative extent of the deficiency. (2) The second point was that in carrying out the antimony trichloride test it was simpler and as, or more, accurate, to take the simple *blue value* in the tintometer, rather than trouble to measure the intensity of either of the absorption bands, since these might fluctuate considerably at the expense of one another or otherwise. One further point was the manner of expressing the results. It seemed preferable to express results as so many "blue units" rather than as a "blue value," as was sometimes done. After all, the latter was only a ratio, and it was much less clumsy to express vitamin *A* results as one would any other analytical results: *i.e.* not as a ratio, but as so many units present in the sample as a whole, or per grm. of the material. This method of expressing results was the one employed by his colleagues at Cambridge, and they were glad to see that it was gradually coming into more frequent use elsewhere. Recent publications from the Nutritional Laboratory, by Dr. Thomas Moore and Mr. Alan Davies, described the technical details of the quite simple procedure adopted there, by which it was easily possible to make analyses of vitamin *A* on as many as four or five specimens per hour, in routine tests. This method was used by them for estimating the vitamin *A* reserves of humans by analysing specimens of liver, *post-mortem*, and several hundred such routine tests had been made in the course of the past year or so.

Another chemical, or physico-chemical test for vitamin *A* was the measurement of the ultra-violet absorption, but, in agreement with what Mr. Bacharach had said, he (Dr. Harris) thought that this was only suitable for use for research purposes and not as a general routine test.

For vitamin *D* (the other principal fat-soluble vitamin) no chemical test of general application to foodstuffs was yet available. For measuring the vitamin *D* (calciferol) content of concentrated medicinal solutions, however, several possibilities offered themselves, of which the most useful and accurate perhaps seemed the measurement of ultra-violet absorption intensity at the specific band.

Coming to the water-soluble vitamins, there were no satisfactory purely chemical tests yet for vitamin B_1. He did not think there would be much delay, however, before one was elaborated, and there was already a semi-chemical test described by Peters and his co-workers, the principle of which was to measure the amount of oxidation induced in a substrate of pigeon brain upon the addition of the vitamin preparation. This was almost a pure chemical test, except for the fact that one of the "reagents" was minced brain tissue of an avitaminous pigeon. Another test of a purely chemical nature, but not truly specific for the vitamin, had been applied for some years past in determining whether a given cereal preparation, such as rice grain, had enough of the germ left in it to render it a good source of the vitamin. This was the phosphoric acid (P_2O_5) determination. This was claimed to give some rough guide to the extent of milling, and, therefore, to the vitamin value; but it was only a makeshift, and he could not claim personal experience of it himself.

For some years past they had been using at the Nutritional Laboratory a quantitative test for vitamin B_1 which, although it was in fact biological, was quite as simple as any chemical test. The principle was to determine the effect on the heart-rate of a deficient rat, and by this simple means an accurately quantitative estimate could be made in the course of a few hours.

Dr. Harris then dealt with the method of estimating vitamin *C* by titration with indophenol. Tracing the historical origin of this test, he said that it started at the Public Analyst's office at Frankfurt-on-Main, where fresh and natural fruit juices had to be distinguished from stale or artificial ones. It was found that this could be done by means of the indophenol reduction value, and after a year or two it was gradually realised that there was considerable parallelism between the reducing value of fresh foods and their vitamin *C* activity. Dr. Harris said that their own quantitative method was based on the reduction of Tillmans' indicator (2–6 dichlorophenol-indophenol), which they had applied in such a way as to make it more specific for the vitamin and suitable for application to various animal, as well as vegetable tissues. The first stage in the process was simply extraction with trichloroacetic acid; this was necessary in order to separate it from the interfering substances present in certain materials, and also to break up cell structure and so get the vitamin suitably into solution. The second stage was to run the acid extract into a measured volume of indicator solution until its colour vanished. By thus working in acid solution they ruled out the interference of such substances as glutathione, which was present in most of the animal extracts rich in vitamin *C* and would otherwise cause serious error, with readings as high as twice or three times the true value. (In a few simple cases, such as lemon juice, this preliminary addition of trichloroacetic acid was not essential, and they might even get a sharper end-point by working in somewhat less acid solution.) The sensitivity of the method was such that when working with materials of the activity, say, of orange juice, they obtained duplicate results agreeing within less than 3 per cent., and with as little as 0·03 ml. of juice for the titration. This micro amount should be compared with the quantity needed for a biological test (at least 400 ml. all told); and the chemical test took only as many seconds to carry out as the biological did days.

As to the specificity of the method, it could be said that it was accurate and quite specific when applied to foodstuffs and vitamin carriers as ordinarily met with; with certain unusual types of material, however, there were one or two special cases where interference might be found. The most important of these, perhaps, was malt extract (Bacharach), which contained a sugar-like reducing substance, and similar products were formed by boiling sugars in slightly alkaline solutions. In dealing with stale or autolysed materials a control test for free cysteine should be made by the Sullivan colour reaction. Tumour tissues might also contain a reducing substance other than the vitamin. But, apart from these one or two special cases, the method was sufficiently specific to have proved its value in a variety of different directions. They had applied it to some forty different natural products and had obtained excellent agreement between the vitamin *C* value thereby calculated from the *ascorbic acid* content and that determined biologically.

The three principal uses of this vitamin *C* titration method seemed to be: (i) for preliminary tests, (ii) for exploratory work (detecting the vitamin in new sources), and (iii) for controlling works operations and concentration processes. In dealing with novel or unusual types of materials it was certainly always advisable to check the results by a biological test. One way, especially, in which the test had been useful was in demonstrating the presence of vitamin *C* in hitherto unsuspected sites, *e.g.* in the suprarenal medulla and cortex, in the lens of the eye, etc.; they had found that rat's suprarenal was amazingly active—about ten times as active as orange juice. All these findings, due to the chemical test, had been confirmed by subsequent biological assays.

The chemical test was also now being used for such routine "works" operations as testing the potency of lemon or orange juice and controlling the manufacture of the evaporated juice; for detecting the loss occurring on canning, preservation and storage; for checking the preparation of active vitamin concentrates; and so forth. It had had interesting results when applied to milk, the vitamin *C* content of which was found to fluctuate in a most erratic way, owing largely, it appeared, to the result of exposure to light (Kon). Again, the test had been very useful in determining the effect of pasteurisation on the antiscorbutic value of milk: traces of copper in the plant were found to have an intensely destructive action. A final illustration was the application of the test to urine. He had found that after a meal containing much vitamin *C* the amount in the urine might rise as high as ten times the normal, and this method they believed had applications, which he was now examining, for diagnostic purposes.

Professor J. C. DRUMMOND directed attention to certain defects in the B.P. procedure for the antimony trichloride test. If the influence of dilution were neglected, abnormal results were obtained. The colours should be matched at the period of maximum intensity, and trustworthy results could be obtained only with the unsaponifiable matter. There was a close correlation between the blue tintometer readings and the spectroscopic test, especially with halibut-liver oils.

Dr. R. J. MCWALTER demonstrated the construction of the Hilger "Vitameter" and the use of the $328 m\mu$ spectrographic band in the estimation of vitamin *A*.

Mr. F. K. DONOVAN referred to the disappearance of vitamin *C* from citrus juices in presence of sulphurous acid. Comparative experiments were being made in Italy, and Mr. Bennett had found that not only did sulphur dioxide prevent the retention of the reducing characteristics associated with antiscorbutic activity, but also that any other preservative which was successful in preventing fermentation entailed a similar loss. Thus, anything that preserved the juice seemed to entail the more or less speedy loss of vitamin *C*.

Dr. KATHARINE COWARD said that by the use of the International Standard for vitamin *A* it was hoped to discover how nearly alike could be the estimations of the vitamin *A* content of one sample of cod-liver oil carried out in the laboratories of different workers. She hoped to publish these results in due course. She thought Mr. Bacharach had made the outlook for the chemical and physical estimations of vitamin *A* in cod-liver oil rather too rosy. She could heartily subscribe to his numerous points, and thought that any one who had followed Mr. Bacharach's analysis of the tests would be able to believe that the comparison of oils by biological tests in various laboratories agreed much better than the comparisons of the same oils by chemical and physical methods in the same laboratories. She, therefore, still pinned her faith to the biological tests.

Mr. E. HINKS referred to the difficulty of the relation between the blue units of the Lovibond instrument and the National Physical Laboratory specification. They were informed by Tintometer Ltd. (ANALYST, 1932, 57, 772), that the limit recommended corresponded to Lovibond blue glass No. 6·0, but it was unfortunate that the relationship was not designated in the Pharmacopoeia. With regard to vitamin *C*, he had observed, when reading Mr. Bennett's paper, that the vitamin-content of preserved lemon juice rapidly diminished: after periods of from ten days to three weeks the titration method showed no vitamin at all. This seemed to be of great significance.

Dr. KON said that he had had very little experience with the estimation of vitamin *A* in cod-liver oil, but had done some work on the vitamin *A* of butters, and had come very definitely to the conclusion that any estimation of vitamin *A* by colour tests on the butter itself was quite impossible. At Reading they had found it was only possible to test the unsaponifiable residue from the butter. They had found that the inhibitor varied according to the season, being present to a larger extent in summer than in winter; therefore, the blue colour test on the butter showed a summer vitamin *A* content lower than the winter value.

The PRESIDENT was sure that all would agree that they had been given valuable information regarding the identification of vitamins. The difficulties surrounding chemical research had been emphasised; not only were the quantities of vitamins in foods extremely small, but quantitative determinations appeared to be almost prevented by reason of other substances present. It was to be hoped that research on chemical tests would continue to be prosecuted. It had been demonstrated that a very considerable amount of research work had been and was being carried out by chemists attached to manufacturing firms, and this should be widely known.

A Modified Micro-Method of Determining Methoxyl and Ethoxyl Groups

BY HOMI RUTTONJI NANJI, PH.D., D.I.C., A.I.C.

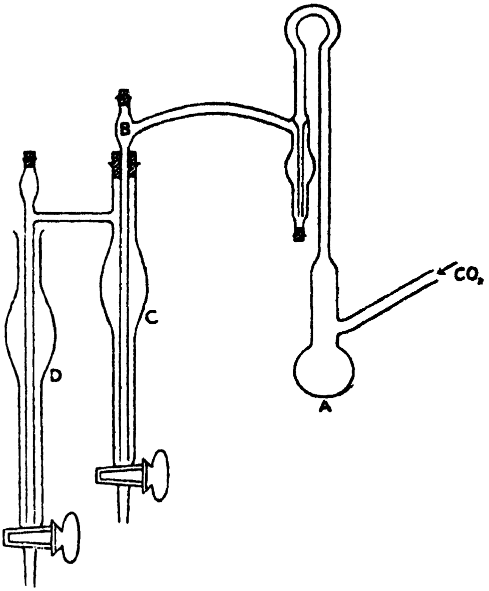
COOL (ANALYST, 1932, 57, 585) recently worked out a method of determining small amounts of ethyl iodide as an indirect determination of cardiac output in man. It consisted in treating the ethyl iodide vapours with chlorine or bromine, whereby the iodide was immediately oxidised to iodate (*cf.* Dumas and Stas, *Ann. Chem. u. Pharm.*, 1840, 35, 162; Dupré and Dupré, *ibid.*, 1855, 94, 165; Friedel, *ibid.*, 1865, 135, 126; Weszelszky, *Z. anal. Chem.*, 1900, 39, 81). The excess of halogen was removed with phenol water, and the iodine, liberated from potassium iodide by the iodate, was determined by titration with sodium thiosulphate.

It was realised that the same principle could be applied with certain modifications in the determination of alkyloxyl groups, which are of such widespread occurrence in plant products.

Vieböck and Schwappach and Vieböck and Brecher (*Ber.*, 1930, 63[B], 2818, 3207) worked out a volumetric iodimetric method on the same principle. They oxidised the methyl iodide by using a solution of bromine in acetic acid solution, and destroyed the excess of bromine by concentrated formic acid. This method was slightly modified by Clarke (ANALYST, 1932, 57, 402). The method afforded little saving of time compared with the old Zeisel method, the limitations of which are given in detail by both the above authors, and may be briefly stated here:—(i) It takes up a considerable time, (ii) The method has to be completely modified if sulphur or phosphorus is present. Further, the various reagents used by Vieböck and Schwappach gave a fairly high blank, and the use of formic acid for removing excess of bromine was not found satisfactory.

The above objections are overcome in the method described below. The principle is that employed by Cool (*loc. cit.*), *viz.* oxidation of alkyl iodide (obtained by heating the alkyloxyl-compound with hydriodic acid) to iodate with bromine water,* removal of excess of halogen by phenol, liberation of an equivalent of iodine from potassium iodide, and titration of the iodine with 0·01 *N* sodium thiosulphate solution.

The apparatus employed for the method is a modification of the old Zeisel apparatus. It consists of an ordinary micro-Zeisel distilling flask (A) described by Pregl (*Quantitative Organic Micro-Analysis*, p. 181 *et seq.*), to which are attached two absorption vessels (C and D) of the form shown in the figure. It is essential that the diameter of the absorption vessels should be such that the leading tube (B) of the distilling flask just goes in. By this means the bubbles of gas are flattened out and more readily absorbed.



The *reagents* required are:—(i) Hydriodic acid, sp.gr. 1·70. (ii) A suspension of purified red phosphorus. (iii) A saturated solution of bromine water; it is advisable to make a fresh solution about every fortnight. (iv) Phenol-water mixture 10 per cent.; this solution keeps indefinitely. (v) Freshly prepared 20 per cent. potassium iodide solution. (vi) A standard (*N*/100) solution of sodium thiosulphate; this may be prepared from time to time by dilution of *N*/10 standard thiosulphate.

ANALYTICAL PROCEDURE.—A few crystals of phenol and 1·5 ml. of hydriodic acid are placed in the distilling bulb, and the washer is filled with phosphorus suspension. About 3 to 4 mgrms. of the dried substance are weighed accurately in a tin-foil cup on a micro-balance and pushed into the distilling flask through the side tube, and the apparatus is connected with a Kipp generator of carbon dioxide. The receivers, containing 4 ml. of bromine water in (C) and 6 ml. in (D), are

* The following equations, given by Clarke, represent the course of the reaction:

$$CH_3I + Br_2 \rightarrow CH_3Br + IBr$$

$$IBr + 2Br_2 + 3H_2O \rightarrow HIO_3 + 5HBr$$

connected in position. A stream of carbon dioxide gas at the rate of 2 bubbles per second is passed through the apparatus. It is important to regulate the rate of flow of gas very carefully, especially at the beginning; otherwise low results may be obtained. The flask is then gently heated by a micro-burner; when the tin-foil has dissolved and the evolution of hydrogen has ceased, the hydriodic acid is heated briskly for a minute, then kept just warm for about 5 minutes, then again heated just to boiling point, and kept warm for a further 5 minutes; this operation is repeated a second time. It is quite unnecessary to keep the acid boiling the whole time. From about 50 determinations it has been observed that the reaction is complete in less than 15 minutes.*

The methyl iodide vapours are completely absorbed in the two receivers. Experiments with one receiver, even with double the column of bromine water, gave low results, showing that the methyl iodide vapours were not completely absorbed in one receiver.

The liquid in both the receivers is then run down through the tap into an Erlenmeyer flask, and the receivers are rinsed two or three times with sufficient water. Ten ml. of well-shaken phenol water† are then added all at once. After two or three minutes, 5 ml. of freshly-prepared potassium iodide solution (20 per cent.) are added, and the liberated iodine is at once titrated with *N*/100 sodium thiosulphate solution.

One ml. of 0·01 *N* sodium thiosulphate solution is equivalent to 0·05171 mgrm. of CH_3O.

The following table summarises the results obtained in a number of determinations:

Substance	Methoxyl found Per Cent.	 present Per Cent.
Vanillin	20·48	20·40
	20·09	
	19·98	
	20·40	
	20·37	
Grape fruit pectin	11·58	11·6*
Commercial citrus pectin	7·95	8·0*
Quinine (hydrated)	8·37	8·20

* The methoxyl values for the samples of grape fruit and citrus pectins, given in the third column, represent those obtained by the old Zeisel method.

The results obtained clearly indicate the accuracy of the method, and its speed is shown by the fact that, after a little practice, four determinations can easily be carried out in two hours.

I am greatly indebted to Dr. Janet W. Brown for carrying out independent determinations to check the method, and also for some useful suggestions.

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* It is, however, to be noted that the compounds tried here are readily decomposed by hydriodic acid, and therefore it is obvious that those which are not readily decomposed would require longer heating, according to the nature of the compound.

† More phenol water should not be added, as it only increases the blank, which, however, is quite negligible with 10 ml. of the mixture. Several blank determinations with 10 ml. of bromine water and 10 ml. of 10 per cent. phenol-water gave values never exceeding 0·1 ml. of *N*/100 sodium thiosulphate solution.

A Rapid Method for the Accurate Determination of Minute Quantities of Nitrite

BY G. GOPALA RAO AND K. MADHUSUDANAN PANDALAI

WE have made a critical examination of several of the methods for the volumetric determination of nitrites, with special reference to their accuracy for small amounts. The method proposed by Lunge (*Ber.*, 1877, **10**, 1074; *Chem.-Ztg.*, 1904, **28**, 501), which consists in the direct titration of an acidified standard solution of potassium permanganate with the nitrite solution in the burette, was found to yield an error of 0·6 to 1 per cent. when applied to *N*/500 nitrite solutions. Kubel (*J. prakt. Chem.*, 1867, **102**, 229) and Fresenius (*Quantitative Chemical Analysis*, Vol. II, p. 196) have advocated using first an excess of acid permanganate, then an excess of a reducing agent such as oxalic acid or ferrous ammonium sulphate, and finishing the titration with permanganate. Our experiments have shown that this method yielded an error of 0·8 per cent. when oxalic acid was used, and an error as high as 4 per cent. with ferrous ammonium sulphate.

Attempts to determine nitrite from the amount of iodine liberated by it from acidified potassium iodide have been made by Davisson (*J. Amer. Chem. Soc.*, 1916, **38**, 1683), Robin (*J. Pharm. Chim.*, 1898, **7**, 575) Winkler (*Chem.-Ztg.*, 1899, **23**, 454), and others. Recently Cool and Yoe (*Ind. Eng. Chem. Anal. Ed.*, 1933, **5**, 112) have reported that the iodimetric methods proposed by Davisson, Robin, Winkler, and Raschig have proved unsatisfactory. We have, therefore, thought it worth while to describe an iodimetric method which was devised by one of us (G. G. R.), and has been used by us for the last two years. This method enables small amounts of nitrite to be determined with considerable accuracy (within ±0·25 per cent.) under ordinary conditions.

The essential reaction in the iodimetric determination of nitrite is:

$$2HNO_2 + 2HI = 2H_2O + I_2 + 2NO.$$

The liberated nitric oxide tends to be oxidised to nitrogen peroxide in the presence of air; this nitrogen peroxide dissolves and liberates more iodine from the acidified potassium iodide. Hence the amount of iodine will be more than corresponds with the equation, and the results for the nitrite will be variable and rather too high. To prevent the results being vitiated by this factor, two conditions must be fulfilled:—(i) There must be no dissolved oxygen in the reaction mixture, and the atmosphere over the solution must consist of carbon dioxide. This condition is secured by causing a rapid stream of carbon dioxide to bubble through the solution for about ten minutes, so that the dissolved oxygen is driven out.

(ii) The nitric oxide must be expelled from the system as it is liberated. For this purpose some sodium bicarbonate is added to the reaction mixture (nitrite solution + potassium iodide + starch) at the outset. Then carbon dioxide is passed through it for ten minutes, after which the solution is acidified with oxygen-free sulphuric acid. The sulphuric acid liberates a large amount of carbon dioxide from the added bicarbonate, and this removes the nitric oxide simultaneously liberated.

With these two conditions thus satisfied, the amount of iodine liberated corresponds exactly with that required by the above equation.

In making a determination, 20 ml. of the nitrite solution are placed in a 250-ml. flask, into which are then introduced about 4 grms. of sodium bicarbonate, 5 ml. of 10 per cent. potassium iodide solution, and a little starch solution. Next, a rapid stream of purified carbon dioxide is made to bubble through this reaction mixture in the flask for about ten minutes to ensure the complete removal of oxygen. The solution is then acidified with 10 ml. of 5 *N* oxygen-free sulphuric acid, and the liberated iodine is titrated with freshly prepared N/500 sodium thiosulphate solution (1 ml. of thiosulphate = 0·000028 grm. of nitrite nitrogen).

The accuracy of the method has been checked with a standard (*N*/500) solution of sodium nitrite prepared from pure silver nitrite. The method yields an average error of 0·25 per cent. With this method it is possible to determine quantities of nitrite nitrogen as small as 0·000028 grm. in 100 ml. of solution.

The following results are typical of those obtained:

Volume of standard *N*/500 sodium nitrite solution Ml.	Volume of 0·00190 *N* thiosulphate solution required Ml.	Amount of nitrite nitrogen, by experiment Grm.	Amount of nitrite nitrogen, theoretical Grm.	Error Per Cent.
20	21·10	0·0005613	0·0005601	+0·21
15	15·80	0·0004204	0·0004204	0·00
10	10·50	0·0002794	0·0002800	−0·21
5	5·30	0·0001410	0·0001400	+0·71
2	2·10	0·00005586	0·00005601	−0·25

In conclusion, one of us (K. M. P.) wishes to thank the Andhra University for giving him facilities to take part in this investigation.

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Notes

The Editor wishes to point out that the pages of the Journal are open for the inclusion of short notes dealing with analytical practice and kindred matters. Such notes are submitted to the Publication Committee in the usual manner.

THE DETERMINATION OF ANTIMONY IN VISCERA AND EXCRETA

A METHOD for the determination of such small quantities of antimony as may be found in viscera and excreta was outlined by Schidrowitz and Goldsbrough (ANALYST, 1911, **36**, 101), and elaborated by Beam and Freak (ANALYST, 1919, **44**, 196). The antimony is deposited on copper, as in the Reinsch test. This deposit is removed by dissolving it in alkaline permanganate solution, the solution is filtered, acidified and treated with sulphur dioxide, any excess of which is removed by boiling, a small quantity of gum arabic solution is added, and the liquid is then diluted to a definite volume. Hydrogen sulphide is passed through the liquid, and, the orange-coloured antimony sulphide remaining in colloidal solution, the determination is made by colorimetric comparison with a standard prepared in the same way.

In expert hands this method gives consistent results, and it was successfully employed in this laboratory by Ibrahim Effendi Idris in carrying out some hundreds of determinations required in a research on the treatment of bilharziasis with antimony compounds (*Beih. Arch. für Schiffs- u. Tropen Hyg. Pathol. u. Therap. Exotisch. Krankeiten*, 1931, **35**, 12).

The technique is, however, somewhat intricate, and there are difficulties which may lead to error in the hands of a worker not thoroughly familiar with the pitfalls.

A much simplified colorimetric method has now been tried and has proved satisfactory, provided that no metal of the second analytical group, other than antimony, is present.

It is based on the process first suggested by Strzyowski* for the destruction of organic matter in preparation for the determination of arsenic, for which purpose we have found the method excellent.

A weighed sample of the tissue to be examined is cut up finely and mixed in a silica basin with sufficient magnesium oxide to give a definitely alkaline reaction. The material is then covered with a saturated solution of magnesium nitrate. In general, 35 to 40 ml. of this solution are sufficient for 100 grms. of animal matter. The mixture is then heated on a sand-bath, with frequent stirring, until the material has dried, charred and begun to whiten. The charred mass may then be crushed with a pestle and afterwards heated more strongly, if necessary over a blowpipe flame. The ash should be quite white. If it is not, it may be cooled, mixed with a concentrated solution of ammonium nitrate, and re-heated until free from nitrates.

The ash, when cold, is moistened with water, and sufficient hydrochloric acid is added to dissolve the magnesium oxide and to give a definitely acid reaction. The solution thus prepared is ready for analysis.

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* "A Simple Method of Ashing for Rapid Determination of Arsenic in Foodstuffs and Animal Materials," *Pharmaz. Post*, 1906, **39**, 977 (quoted by Autenrieth, *Laboratory Manual for the Detection of Poisons and Powerful Drugs*, sixth American edition, p. 493).

The advantages of this technique are:—(i) The arsenic or antimony is converted into the non-volatile pyro-arsenate or pyro-antimonate of magnesium, which can be incinerated without appreciable loss.

(ii) Magnesium nitrate decomposes, when heated, into magnesium oxide and oxides of nitrogen, the residue being free from nitrates and nitrites.

For the determination of arsenic by the Marsh–Berzelius or the Gutzeit method no further treatment is required, except the addition of stannous chloride to reduce the arsenic to the arsenious condition.

Before the determination of antimony, however, it is necessary to remove iron. The solution is, therefore, diluted with distilled water and saturated with hydrogen sulphide. The precipitate is filtered off, washed in the usual way, and dissolved in the minimum quantity of hot concentrated hydrochloric acid. This solution is diluted with distilled water and re-filtered, if necessary, to remove fragments of filter paper, and, after the addition of gum arabic solution (1 ml. of a 5 per cent. solution being sufficient for 100 ml. of liquid), the solution is made up to a definite volume. Hydrogen sulphide is again passed through the liquid, and the colour is compared in a Duboscq colorimeter with that of a standard of approximately equal concentration.

For the preparation of the standard solution it is unnecessary to use magnesium pyro-antimonate, as was shown by the following experiment:—One ml. of a 5 per cent. solution of tartar emetic was mixed with magnesium oxide and magnesium nitrate solution, evaporated to dryness, and the residue incinerated. The ash was dissolved in the minimum quantity of hydrochloric acid, gum arabic solution was added, and the volume was made up to 1 litre with distilled water. A second solution was made by diluting 1 ml. of the 5 per cent. tartar emetic (slightly acidified and mixed with gum arabic) to 1 litre. Equal aliquot parts of the two solutions were saturated with hydrogen sulphide, and the colours were compared; they were identical.

This concentration (0·005 per cent. tartar emetic) was found to give a colour intensity quite suitable for colour comparison.

In a forensic case tartar emetic had been injected intravenously in mistake for glucose. We had no exact knowledge of the quantity injected, but it was stated that 50 ml. of a 5·6 per cent. solution had been measured out for injection by gravity. The patient almost immediately showed signs of collapse, and the hypodermic needle was withdrawn. Unfortunately the quantity of fluid not injected was unknown. The patient lived for about four hours, and, after the autopsy, samples of blood and liver were sent for analysis. Two samples of the liver, weighing, respectively, 50 grms. and 20 grms., were examined, and the results of analysis were identical, *viz.* 25 mgrms. per 100 grms., calculated as tartar emetic. A sample of blood (50 ml.) treated in the same way was found to contain 2 mgrms. The quantities estimated for 1500 grms. of liver and 5000 ml. of blood were, therefore, as follows:

Liver.—375 mgrms. (as tartar emetic) or 140 mgrms. as metallic antimony.

Blood.—200 mgrms. (as tartar emetic) or 74 mgrms. as metallic antimony.

Khalil (*loc. cit.*) states that the accumulation of 200 mgrms. of antimony in the adult human body is liable to cause death.

(*Cf.* Clarke, ANALYST, 1928, **53**, 373; 1929, **54**, 23; and Evans, *ibid.*, 1922, **47**, 1; 1927, **52**, 565.

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THE DETECTION OF COPPER BY MEANS OF *p*-PHENYLENEDIAMINE

When a few drops of a mixture of 5 ml. of potassium thiocyanate solution and 2 or 3 drops of an aqueous solution of *p*-phenylenediamine are added to a solution of a copper salt a black precipitate of copper thiocyanate phenylenediamine is produced. The test is capable of detecting 1 part of copper in 100,000.

The black copper precipitate is formed in ammoniacal or neutral solutions; it is soluble in acid, giving a black solution.

No precipitate is given by cobalt, manganese, iron, magnesium, aluminium, chromium or nickel. Cadmium and zinc form white precipitates soluble in acid and ammoniacal solutions. Mercury gives a gray precipitate soluble in ammoniacal, but insoluble in acid solutions. Silver gives a white precipitate soluble in acid, but insoluble in ammoniacal solution.

With the exception of silver, therefore, all the common metals may thus be separated from copper.

Following the general scheme of qualitative analysis, we shall have, if copper and cadmium are present, an ammoniacal solution of cadmium and copper salts in Group II. To this solution are added 2 or 3 drops of a solution of, say, 5 ml. of saturated potassium thiocyanate solution and 2 or 3 drops of an aqueous solution of *p*-phenylenediamine. A black precipitate of the copper salt is formed, but the cadmium is not precipitated. The precipitate is filtered off, and hydrogen sulphide is passed into the filtrate; a yellow precipitate indicates cadmium.

The copper compound formed is undoubtedly co-ordinated, and the diamine has been proved to be linked to the copper ion. The compound contains 25·08 per cent. of copper.

Further work is being carried out with this and similar co-ordination compounds.

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AN INEXPENSIVE AND ECONOMICAL WARM ROOM

The chemist in a small factory often wishes to test at different temperatures the products which he is examining, but, having no hot room in which to place any bulk of material, has to rely upon small-scale tests in the ordinary incubator. The apparatus here described is an inexpensive substitute for a hot room. The hot chamber, which has an internal capacity of about 30 cb. feet, is made of ordinary tongue-and-grooved one-inch planks and is double-walled, the space between the inner and outer walls being filled with broken cork and sawdust. The top and the door are also insulated. The heating system consists of two 250-watt tubular lamps which are fitted with a temperature-control regulator, the thermostat being at the top of the chamber. (This apparatus is shown in Gallenkamp's catalogue—B.3767.) The temperature at various parts of the chamber shows slight but uniform variations, the following figures, which were taken over a period of one month, being typical:

Position of thermometer	Maximum °F.	Minimum °F.
Top	83	78
Middle	84	79
Bottom	88	81

During the Christmas holidays the chamber remained closed for a period of 136 hours, and the temperatures at the above positions were 82° to 79°, 83° to 81°, and 88° to 83° F., respectively. During this period the current used was only 25 units, which gives a daily consumption of about 4½ units. I have used this type of chamber at temperatures between 80° and 105° F. with complete success.

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A NICKEL VESSEL FOR STORING STANDARD CAUSTIC ALKALI SOLUTIONS

The difficulty of keeping standard caustic alkali solutions is well known. Waxed vessels are often employed, but have the disadvantage that the wax peels away after prolonged contact with the solution.

I have found a vessel of heavy-gauge pure nickel to be very convenient for preserving *N*/10 caustic soda solution. The vessel, which was made to specification by a firm in the trade, has the approximate shape and dimensions of a Winchester quart bottle. The mouth is fitted with a rubber bung carrying the usual soda-lime tube and a supply tube of seamless Monel-metal for the burette.

After a period of eight months the alkali was perfectly clear and its normality was unchanged. After each titration the alkali remaining in the burette is always allowed to run back immediately into the nickel vessel.

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Sub-Committee on the Determination of Unsaponifiable Matter in Oils and Fats, and Unsaponified Fat in Soaps

NOTE ON THE B.P. LIMITS FOR "FREE FAT" IN SOAPS

In the 1932 B.P. the limit for "free fat" for Sapo Animalis, Sapo Durus and Sapo Mollis corresponds to 0·5 per cent. The method described for free fat determination returns unsaponifiable matter, as defined in the Report of the Sub-Committee for the Determination of Unsaponifiable Matter, etc., in The Analyst (1933, **58**, 203), as well as any free unsaponified saponifiable material. Hence, it is clear that the limit specified should be such as to include at least the maximum amount of unsaponifiable matter which is likely to be present in the oil from which it is specified that the soap should be made. The limit, however, should not greatly exceed such an amount, since the object of the test is to avoid the presence of more than a minimum of unsaponified saponifiable matter, as well as to detect any undue amount of unsaponifiable matter.

Recent determinations of the unsaponifiable matter in genuine samples of olive oil show that this oil may contain up to 1·25 per cent. of unsaponifiable matter when examined by the method given in the B.P. This quantity of unsaponifiable matter would correspond to 0·88 per cent. returned by the B.P. test as "free fat" on a soap containing 70 per cent. of fatty acids. It is recommended, therefore, that the limit of "free fat" specified in the B.P. for Sapo Durus should be altered to correspond to 1·0 per cent., and that for Sapo Mollis to 0·7 per cent., the latter being calculated on a basis of 44 per cent. of fatty acids.

Further, the unsaponifiable matter of purified solid animal fats, such as tallow, may be 0·7 per cent. or rather more. Hence, the free fat limit of 0·5 per cent., specified in the B.P. for Sapo Animalis, may not be attainable, and therefore it is suggested that the limit in this case should be fixed at 0·7–0·8 per cent.

(*Signed on behalf of the Sub-Committee*) L. V. Cocks (*Chairman*)
Norman Evers (*Hon. Secretary*)

Report of the Essential Oil Sub-Committee to the Standing Committee on Uniformity of Analytical Methods

REPORT No. 11

THE DETERMINATION OF ALDEHYDES OTHER THAN CITRONELLAL*

THE investigations of the Essential Oil Sub-Committee have shown that, for the determination of aldehydes in essential oils, the hydroxylamine method offers considerable advantages over the commonly employed bisulphite and neutral sulphite methods. The results obtained by different operators are more concordant, and the method is less affected by impurities in the oils themselves. Thus, in the bisulphite and neutral sulphite methods, impurities such as water-soluble organic acids, and adulterants such as alcohol, would be recorded as aldehyde, while the addition of substances such as resin frequently results in the formation of an emulsion and renders an accurate reading of the line of demarcation between the bisulphite solution and the non-aldehyde portion of the oil a matter of considerable difficulty.

The hydroxylamine method, on the other hand, is a definite determination of aldehydic (or ketonic) substances, and is affected very little, if at all, by the presence of traces of free organic acids such as are frequently present in essential oils, as these are usually without action on the indicator used in the method.

A further advantage of the hydroxylamine method is that a small quantity only of the oil is required and the determination can be completed in a much shorter time.

Particular attention must be paid to the adjustment of the reagent and to the end-point of the reaction, and, as both these conditions depend on the change in colour of methyl orange from red to yellow, it is obvious that the operator's eyes must not be insensitive to this colour change.

The Sub-Committee recommends the following method for the determination of aldehydes in oil of cassia, oil of cinnamon, oil of lemongrass, oil of orange, oil of bitter almond, oil of cherry-laurel, oil of cummin (cumin) and terpeneless and sesquiterpeneless oils of lemon and orange.

The following solutions are required:

Indicator Solution.—A 0·2 per cent. solution of pure methyl orange in alcohol (60 per cent. v/v).

N/2 Alcoholic Potash.—Prepared with alcohol (60 per cent. v/v) and standardised against *N*/2 hydrochloric acid, using methyl orange as indicator, and running the alkali into the acid until the full yellow colour is obtained.

N/2 Hydroxylamine Hydrochloride.—Dissolve 3·475 grms. of pure hydroxylamine hydrochloride in 95 c.c. of alcohol (60 per cent. v/v), add 0·5 c.c. of the indicator solution, adjust to the full yellow colour of the indicator with the *N*/2 alcoholic potash, and make up to 100 c.c. with alcohol (60 per cent. v/v).

The alcohol used throughout must be free from aldehydes and ketones.

The full yellow colour of the indicator may be defined as that colour which is not changed by the further addition of alkali. The correct adjustment of the reagent should be confirmed in the following manner:

Place 10 c.c. in each of two tubes, and to one tube add 1 drop of *N*/2 alcoholic potash; no change in colour should be observed. To the other tube add 1 drop of *N*/2 hydrochloric acid; a slight change in colour towards orange should be produced.

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* See Report No. 10.

METHOD OF DETERMINATION.—Weigh out exactly, into a glass-stoppered tube—approximately 150 mm. long by 25 mm. in diameter—a suitable quantity* of the oil, add 5 c.c. of benzene and 15 c.c. of *N*/2 hydroxylamine hydrochloride reagent. Shake vigorously and titrate with the *N*/2 alcoholic potash until the red colour changes to yellow. Continue the shaking and titrating until the full yellow colour of the indicator is permanent in the lower layer after shaking vigorously for two minutes and then allowing to stand for the liquids to separate. The reaction is slow towards the end, but should be complete in about 15 minutes.

The result should be confirmed by a second determination, and the first titration liquid *plus* a slight excess of alcoholic potash (0·5 c.c.) should be used as a colour standard for the end-point of the second titration.

The number of c.c. of *N*/2 alcoholic potash used multiplied by the correcting factor 1·008, by the factor for the appropriate aldehyde, and by 100, and divided by the weight of oil taken will give the percentage (by weight) of aldehydes, calculated as that aldehyde, present in the oil.

The following factors should be used for the aldehydes:—

Benzaldehyde*	0·053
Cinnamic aldehyde	0·066
Citral	0·076
Cuminaldehyde	0·074
Decylic aldehyde	0·078

* In the determination on benzaldehyde-containing oils, allowance should be made for the amount of acid titratable to methyl orange.

The correcting factor is necessary, owing to the fact that the end-point of the titration occurs at a p_H different from that of normal hydroxylamine hydrochloride.

The purpose of the benzene is twofold; first, it acts as a solvent for the oil and, in the subsequent shaking, aids in producing a fine dispersion of oil globules in the mixture and thus promotes surface contact between the reacting liquids; and, secondly, it is a solvent for the non-aldehyde portion of the oil and prevents the inherent colour of this from interfering with the colour of the indicator in the dilute alcoholic solution.

The Sub-Committee recommends that, in recording results, the following type of wording should be used:

Total aldehydes by the hydroxylamine method, calculated as citral (or other aldehyde) per cent. by weight.

Determinations made by members of the Sub-Committee lead us to the opinion that the maximum variation with this method should not exceed ± 1 per cent. The following tables show the results obtained by members of the Sub-Committee on samples circulated for collective testing. It should be noted that the results reported for the bisulphite method were obtained by members, each using his own technique.

RESULTS OF THE DETERMINATION OF CINNAMIC ALDEHYDE IN AN ARTIFICIALLY PREPARED MIXTURE

The cinnamic aldehyde used contained 97·6 per cent. of pure cinnamic aldehyde and 2·0 per cent. of free acid, calculated as cinnamic acid. It was completely soluble in sodium bisulphite solution. The mixture was made by diluting 60 parts by weight of the aldehyde with 40 parts by weight of copaiba oil, and thus contained 58·6 per cent. by weight of cinnamic aldehyde.

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* About 1 grm. of oil of cinnamon, oil of cumin or oil of lemongrass; about 0·8 grm. of oil of cassia and about 0·6 grm. of oil of bitter almond, oil of cherry-laurel, terpeneless and sesquiterpeneless oils of lemon and orange, and from 5 to 10 grms. of oil of orange.

Sub-Committee Member	Hydroxylamine method Per cent. by weight	Bisulphite method		
		Per cent. by volume	=	Per cent. by weight
1	58·1	58·0		61·9
	58·2			
2	57·2	59·5		63·5
	58·0			
3	57·1	58·5		62·4
4	57·3	60·0		64·1
	57·4			
	58·0			
5	57·8	56·9		60·8
6	58·8	57·0		60·9
	58·8	57·0		60·9
7	57·4	58·0		61·9
	58·3			
8	57·7	56·6		60·5
9	58·0	57·0		60·9
	57·9			
10	57·6	58·0		61·9
Variation	57·1 to 58·8	56·6 to 60·0		60·5 to 64·1
Mean	57·9	57·9		61·8

CINNAMIC ALDEHYDE IN CRUDE OIL OF CASSIA

Sub-Committee Member	Hydroxylamine method Per cent by weight	Bisulphite method Per cent. by volume
1	74·8	82
2	74·9	81
	75·1	82
3	76·0	82
	75·5	82
	74·9	
4	75·4	80·5
	75·5	80·5
5	75·2	80
	75·4	
	75·3	
	75·3	
6	75·2	81
	75·1	82
	74·9	
7	75·8	80·5
	76·3	
	76·1	
8	76·2	79·5
		79·5
9	75·8	81
	76·3	82
Variation	74·8 to 76·3	79·5 to 82
Mean	75·5	81

CITRAL IN OIL OF LEMONGRASS

Sub-Committee Member	Hydroxylamine method Per cent. by weight	Bisulphite method Per cent. by volume
1	75·4	80·1
		81
2	74·7	77
	74·3	78
3	75·3	79
	74·85	78
	75·25	
	74·7	
4	74·6	73·5
	74·0	73·5
5	75·0	76·5
	75·0	(75·5 neutral)
	74·9	
	74·7	
6	74·1	74
	74·0	75
	74·2	
7	75·5	74·6
	75·0	74·6
	75·1	(75 neutral)
	75·3	
	74·7	
8	74·4	78
		78·5
9	75·4	77
	75·8	78
Variation	74·0 to 75·8	73·5 to 81
Mean	74·84	75·66

(*Signed*)
W. H. Simmons (Chairman), C. T. Bennett, S. W. Bradley, L. E. Campbell, Thos. H. Durrans, T. W. Harrison, Ernest J. Parry, C. Edward Sage, T. Tusting Cocking (Hon. Secretary).

Official Appointments

THE Minister of Health has approved the following appointments:

FREDERICK WILLIAM EDWARDS as Public Analyst for the Metropolitan Borough of Hammersmith, in place of P. A. E. Richards, resigned, December 31, 1933 (January 6th).

ERNEST VICTOR JONES as Public Analyst for the Borough of Newcastle-under-Lyme, in place of A. E. Johnson (deceased) (January 6th).

ERNEST VICTOR JONES as Public Analyst for the Borough of Stoke-on-Trent, in place of A. E. Johnson (deceased) (January 26th).

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(*From the beginning of the year* 1921 *to date*)

XI ANTIMONY

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Ministry of Health

SALE OF FOOD AND DRUGS ACT

EXTRACTS FROM THE ANNUAL REPORT FOR 1932–1933, AND ABSTRACTS OF REPORTS OF PUBLIC ANALYSTS FOR THE YEAR 1932[*]

OF the 137,981 samples of food and drugs submitted to Public Analysts in 1932, 7019, or 5·1 per cent., were reported as adulterated or not up to standard. This is a slight increase as compared with 4·6 and 4·8 per cent., respectively, for the two previous years. The practice in certain areas is that all the milk samples are first examined by the sampling officers, and consequently only samples believed to be adulterated are sent to the analyst. Attention is called to the risk in these areas of failing to detect some of the less common forms of adulteration.

PRESERVATIVES.—The number of infringements of the Regulations reported was 549; in 200 cases prohibited preservatives were found in foods, such as boron in sausages, cream, margarine, caviare, and cake; formaldehyde in milk; sulphur dioxide in sweets, minced and potted meat, desiccated soups and pepper, and salicylic acid in a few samples of non-alcoholic wine, lime juice cordial, jam and mushroom ketchup. In 131 samples of such foods as raisins, sultanas, jam and raisin wine, preservative was in excess of the amount permitted. A "dusting powder," consisting of a mixture of borax and boric acid, was used for sausages.

MILK.—Of the 72,940 samples of milk examined, 5307, or 7·3 per cent., were reported against, the corresponding percentages for 1930 and 1931 being, respectively, 6·6 and 6·4. Of the 893 "appeal-to-cow" samples, 41·2 per cent. were below the presumptive standard of the Sale of Milk Regulations, 1901, but these samples were taken at farms the milk from which had previously been sampled, and found to be below standard. In several cases of adulteration with water, convictions were obtained. Visible dirt was present in 21 samples, added colouring matter in 12, and formaldehyde in 13. Of graded milk, 31 samples were deficient in fat or non-fatty solids, and 13 samples of skimmed milk in non-fatty solids.

CONDENSED AND DRIED MILK.—Of 1198 samples of condensed milk, 16 were reported against, 5 were deficient in milk solids-not-fat, 1 in milk-fat, and 2 in both.

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[*] To be obtained from H.M. Stationery Office, Adastral House, W.C.2. Price 4d. net.

CREAM.—Forty-three of 2207 samples of cream were reported against; 24 (mostly tinned cream) were deficient in fat, 13 contained boron preservative; 4 samples sold as cream were re-constituted cream; 1 sold as dairy cream was sterilised cream, and one sample consisted mainly of vegetable oil.

BUTTER AND MARGARINE.—Of the 9707 samples of butter reported upon, 65 contained excess of water, 13 foreign fat, and 4 excess of free fatty acid. One sample sold as fresh butter contained salt, and one consisted entirely of margarine. Twenty-five of 3294 samples of margarine contained excess water; 6 boron preservative; 11 were incorrectly labelled, and one, containing only 2 per cent. of butter, was sold as "margarine butter."

LARD AND OTHER FATS.—Nine of 2727 samples of lard were reported against (4 consisting of beef or other foreign fat, 3 of partly foreign fat, 1 contained excess of free fatty acid and one sodium bicarbonate); 28 of 363 samples of suet (8 samples sold as suet contained starchy materials and 20 of shredded suet contained excess of such material or were incorrectly labelled); 7 of 628 samples of dripping contained either excess of water or fatty acid or rice flour (1 sample) or 30 per cent. pork fat (1 sample).

CHEESE.—Of the 1377 samples of cheese examined, 10 "cream cheeses" were ordinary cheeses made from whole milk, 1 was decomposed, 5 (sold as Cheshire cheese) were deficient in fat and made from partly skimmed milk. In only 2 cases was contamination by tin reported. In one of these 14 grains per lb. were present, and the vendor was prosecuted and fined.

BREAD AND FLOUR.—One sample of 227 breads examined contained 0·225 per cent. of lactic acid and was mouldy. Five samples of flour (all self-raising) of 1265 analysed, were reported against, 1 for containing calcium phosphate, 2 sulphate of lime, and 2 for being ordinary white flour. One contained weevils, caterpillars, etc.

JAMS AND MARMALADE.—Eighty-six of 1759 samples examined were reported against—53 for being deficient in fruit or other soluble solids or not being in accordance with the label. Twenty-nine samples contained an excess of preservative; 1 a prohibited preservative, and 2 marmalades, labelled free from preservative, contained preservative.

VINEGAR.—Of 1856 samples of vinegar, 114 were deficient in acetic acid; 37 samples, sold as "malt," "grape" or "table" vinegar, were wholly or partly artificial vinegars; one sample contained lead and another a trace of oil.

SPIRITS AND BEER.—Under 65 per cent. of proof spirit was reported in 7 brandies, 41 gins, and 98 whiskies of a total of 2013 samples examined, and 6 samples, sold as "wine and brandy," "wine and whisky," or "rum punch," were over 60 degrees under proof, and had misleading labels. A sample of rum was 41·5 degrees under proof. Six samples of beer (of 440 examined) contained arsenic in excess of 1/100 grain per gal.; 5 contained traces of lead, and 2 samples, sold as "special Lager mild ale" and "black malt beer," respectively, contained so little alcohol as to be practically non-alcoholic drinks.

MISCELLANEOUS ARTICLES OF FOOD.—Some 30,000 other samples of food were examined. Sugar was found adulterated with salt, ground rice, desiccated coconut and lard; one sample contained 33·66 per cent. of sodium thiosulphate; 23 samples of cinnamon and mixed spice were adulterated with silicious matter. Mustard was reported to be adulterated with flour and the ground skins of mustard seed, and samples of pepper contained 75 per cent. of rice starch. Contamination with arsenic was reported in cocoa, potted shrimps, apples, sweets, black beer and baking powder; tinned sardines and cocoa were contaminated with lead; cider with lead and copper; dried peas, mincemeat, mushrooms-in-butter, and Worcester sauce with copper, and tin was found in various tinned foods. "Pure chocolate cream Easter eggs" consisted of a filling of sugar and glucose and gelatin covered with chocolate, itself consisting of hardened vegetable oil (probably coconut), cornflour and cocoa husk. "Honey and butter rock" was reported to contain no honey.

DRUGS.—Of 5606 samples of drugs, 209 were adulterated or below standard and included ground ginger, camphorated oil, lozenges, medicated tablets, ointment, liquorice powder and iodine. Sixteen samples of camphorated oil were deficient in camphor up to 48·5 per cent., and one sample was stated to contain 61 per cent. of synthetic camphor. Bismuth lozenges contained no calcium carbonate or contained French chalk; aspirin tablets were deficient in aspirin, lime water in lime, borax and honey was devoid of borax, and creosote ointment was deficient in creosote. A cream of tartar was 100 per cent. arrowroot. Nerve and digestive tablets were 100 per cent. deficient in potassium iodide, samples of cod-liver oil emulsion with hypophosphites were found to be deficient in hypophosphites and in oil, and Seidlitz powders contained less tartaric acid than is prescribed in the British Pharmacopoeia. Excess of lead was present in Epsom salts and tartaric acid, and excess of arsenic in borax; peach or apricot kernel oil was supplied for almond oil, and ground ginger contained preservative.

D. G. H.

Department of Scientific and Industrial Research

THE MEASUREMENT OF HUMIDITY IN CLOSED SPACES *

THIS is a new edition of a Report, originally published in 1925, and now revised and much extended by Dr. Ezer Griffiths, incorporating the results of further experiments carried out by himself and Mr. J. H. Awbery. It is introduced by a prefatory note by Sir J. A. Ewing explaining its scope.

MEASUREMENT OF HUMIDITY.—The Report points out that there are three methods in common use—the wet-and-dry bulb hygrometer invented in 1813; the dew-point apparatus dating from 1827; and the hair hygrometer used as far back as 1783—and states that "no fundamentally new method of hygrometry has been introduced, in spite of the immense amount of attention which has been given to the subject, during the past one hundred years." While the report deals mainly with the three classical methods, it indicates how much has been done towards improving the accuracy of these methods and in devising automatic, distant-reading and recording apparatus for use in special industrial applications, such as the determination of humidity in a closed store, in a stack of fruit, or in other inaccessible places.

WHIRLING THERMOMETERS.—With the wet-and-dry bulb hygrometer, or psychrometer as this instrument is sometimes called, the humidity is determined from the difference in the reading of two thermometers, the bulb of one of which is covered with a wet muslin sheath. The report lays stress on the importance of keeping the air moving past the thermometers. This may be done either by whirling the thermometers or by drawing air through a tube in which they are placed. To make the instrument distant-reading, the ordinary mercury thermometers may be replaced by electrical thermo-couples.

THE DEW-POINT HYGROMETER.—The dew-point apparatus depends on finding to what temperature a surface must be cooled for dew to be deposited on it. In

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* Food Investigation Special Report No. 8. (Revised Edition, 1933.) Pp. viii + 70, with 49 figures. H.M. Stationery Office, Adastral House, Kingsway, London, W.C.2.

its simple form, therefore, the method depends primarily upon the observer's visual acuteness in detecting a trace of dew. In distant-reading instruments some other method of detecting the presence of dew is necessary. In one instrument, radiation reflected by a polished surface is arranged to produce an electric current by falling on a thermo-couple. The formation of dew changes the reflecting power of the surface and thus alters the current. The observer, therefore, instead of watching for the dew to form, watches for the movement of the pointer of a sensitive galvanometer. Another instrument uses a photo-electric cell. Light is reflected from the cooled surface, and the photo-electric cell is so placed that some of the light scattered from this surface when dew begins to form on it falls on the cell and reduces its resistance. An electric circuit connected with the cell is so arranged that clicks are produced in a telephone in the circuit when there is no dew, but cease when dew is formed.

THE HAIR HYGROMETER.—The hair hygrometer depends on the fact that hair, and some other organic materials, lengthen and shorten as the humidity of the surrounding atmosphere increases and decreases. These changes of length may be communicated to a pointer moving over a scale or over a recording drum. The materials studied for humidity work include specially prepared bundles of human hair, single horse-hairs, fibres of raw silk and of artificial silk, strips of goldbeaters' skin, jewellers' tissue paper and mohair. The Report states that a single horse-hair is remarkable for the closeness with which its indications are repeated when it is taken through several cycles of humidity, and that goldbeaters' skin is remarkable for the rapidity with which it reaches equilibrium when the humidity is rapidly changed.

OTHER FORMS OF HYGROMETER.—A further method of measuring humidity that has been tried consisted in finding the variation with humidity of the refractive index of a prism to the surface of which a film of glycerin had been applied. In another method the effect of humidity in changing the temperature, and therefore the resistance, of cotton-covered nickel wire was used, and another interesting instrument, termed the fog-formation hygrometer, was constructed as follows:—Some of the air under examination was drawn into a vessel and suddenly expanded in another vessel at a lower pressure. Ordinarily the water vapour in the air produces a dense fog as the result of the cooling of the air by expansion. The pressure of the vessel into which the air expanded was adjusted, however, until the fog was either just visible or just invisible. This pressure is directly related to the humidity.

Yet another method considered in the report depends on the fact that the loss of heat from a hot wire depends on the conductivity of heat of the surrounding atmosphere. The thermal conductivity of hydrogen is, for example, six times that of air. Accordingly, this method has had an extensive application in recorders of the amount of hydrogen and carbon dioxide present in a particular atmosphere. The report refers to the fact that Koepset claimed for a German apparatus made on this principle that it can easily detect the presence of 0·001 per cent. of hydrogen (*Ber. physik. Ges.*, 1908, **10**, 814); a simple British instrument on these lines was developed during the war for measuring the permeability of balloon fabrics to hydrogen (Shakespear, *Proc. Phys. Soc.*, 1921, **33**, 168). Unfortunately, the change in thermal conductivity in air, due to the presence of water vapour, is not sufficiently marked to make this generally as accurate as the ordinary methods for measuring humidity. The Report adds, however, that the method may prove of great service for measurements of humidity at temperatures beyond the range of the classical methods.

BIBLIOGRAPHY.—The classified bibliography, occupying 5 pages, contains 106 references and includes most of the important papers bearing on the present Report.

The Pharmaceutical Society of Great Britain Codex Revision Committee

THE following reports have been published by direction of the Council of the Pharmaceutical Society.* In each instance the Editor of the *British Pharmaceutical Codex* (17, Bloomsbury Square, W.C.1), will be pleased to receive any observations on points relating to them.

REPORT OF PHARMACOGNOSY SUB-COMMITTEE.—This gives a summary of the principal standards for Crude Vegetable Drugs recommended by the Sub-Committee and accepted provisionally for inclusion in the British Pharmaceutical Codex, 1934. It comprises 100 crude drugs arranged in alphabetical order. It is published at 2s.

REPORT OF "ACTION AND USES" SUB-COMMITTEE.—In addition to the revision of the "action and uses" sections of about one thousand monographs, the Sub-Committee, assisted by a number of specialists, has supplied the descriptive portions for about fifty drugs, mostly of animal origin, including antitoxins, toxins, and gland products.

In this summary are given certain sections from the descriptions recommended and the standards proposed for the more important of these substances, in the hope that they may be of interest to manufacturers and others. For the substances which are not included in the British Pharmacopoeia, the B.P.C. standard for substances controlled by the Therapeutic Substances Act will be the same as the standard laid down by the regulations made under that Act. The Report is published at 1s. 6d.

REPORT OF PHARMACEUTICAL CHEMISTRY SUB-COMMITTEE.—The chemical substances for inclusion in the next issue of the British Pharmaceutical Codex fall into three groups. First, those for which a standard is laid down in the British Pharmacopoeia and for which the Sub-Committee has provided only additional and useful descriptive matter. Secondly, those for which the Sub-Committee has worked out a series of tests to form a British Pharmaceutical Codex standard for the substance. Thirdly, those for which the Sub-Committee has not recommended a particular standard and which are included to provide necessary and useful information. It is to the more important substances of the second group that this summary relates.

The Sub-Committee recommends that the methods of procedure for limit tests and other tests which form tests of purity, unless directed otherwise, shall be the same as those of the corresponding tests of the British Pharmacopoeia.

REPORT OF PHARMACY SUB-COMMITTEE.—This contains a summary of the principal new or revised formulae recommended by the Sub-Committee for inclusion in the British Pharmaceutical Codex, 1934. For many of the preparations the Sub-Committee has worked out tests, and has recommended that these should be included to form a B.P. Codex standard for the preparation. The inclusion of alcohol limits for the concentrated infusions, spirits and tinctures is also recommended. The Sub-Committee hopes that it will be possible to obtain the permission of the Board of Customs and Excise to use methylated spirit in making preparations which are not to be taken internally.

The formulae are expressed in both metric and Imperial systems. The Report is published at 2s. 6d.

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* Published by the Pharmaceutical Press, 23, Bloomsbury Square, London, W.C.1.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs Analysis

Chemical Study of Tomato Juice. C. F. Poe, A. P. Wyss, and T. G. McEver. (*J.A.O.A.C.*, 1933, 16, 624–627.)—Raw and cooked tomato (Colorado) juices, containing practically all the liquid and pulp, show virtually no differences in composition, refractivity, or specific gravity, if prepared from the same sample. Analysis of 8 samples of home-canned tomato juices, containing no added salt, gave the following minimum, average, and maximum percentage results: Total solids, 5·02, 5·71, 6·48; soluble solids, 4·66, 5·31, 6·10; insoluble solids, 0·32, 0·43, 0·55; per cent. of total "serum" solids soluble in 95 per cent. alcohol, 53·98, 59·47, 66·12; ash, 0·41, 0·47, 0·51; water-soluble ash, 0·39, 0·44, 0·47; alkalinity of water-soluble ash in c.c. of N hydrochloric acid per 100 grms. of juice, 4·65, 5·90, 6·53; salt, 0·06, 0·09, 0·12; acetic acid as ml. of 0·1 N sodium hydroxide per 100 grms. of juice, 0·61, 0·71, 0·77; fixed acid, expressed similarly, 44·1, 63·8, 79·1; fixed acid as malic acid, 0·30, 0·43, 0·53; reducing sugar after inversion, 2·44, 3·08, 3·38; n_D at 20° C., 1·3400, 1·3412, 1·3424; immersion refractometer reading at 20° C., 32·8, 35·9, 39·1; sp.gr. at 20° C., 1·0209, 1·0232, 1·0267.

The corresponding results for 8 samples of home-canned juices containing salt were: Total solids, 6·37, 7·24, 7·90; total solids, salt-free, 5·22, 5·91, 6·42; soluble solids, 5·99, 6·82, 7·44; insoluble solids, 0·33, 0·45, 0·55; per cent. of total "serum" solids soluble in 95 per cent. alcohol, 54·93, 58·27, 64·12; salt-free ash, 0·34, 0·42, 0·50; salt, 0·62, 1·33, 1·74; acetic acid, as above, 0·58, 0·75, 0·83; fixed acid, as above, 55·0, 69·3, 81·2; fixed acid as malic acid, 0·37, 0·46, 0·54; reducing sugars after inversion, 2·26, 2·90, 3·28; n_D at 20° C. (or corrected for salt), 1·3421 (1·3403), 1·3436 (1·3414), 1·3448 (1·3421); immersion refractometer reading at 20° C. (or corrected for salt), 39·0 (33·2), 42·4 (36·3), 45·3 (38·4); sp.gr. at 20° C. (or corrected for salt), 1·0278 (1·0204), 1·0328 (1·0235), 1·0356 (1·0255).

Indications of adulteration may be obtained from determinations of: Total solids and insoluble solids, on the whole juice; solids, water-soluble solids, ash, alkalinity of the ash, immersion refractometer reading, volatile acids, and reducing sugars, all on the "serum." T. H. P.

Composition of the Egg Plant Fruit at Different Stages of Maturity. C. W. Culpepper and H. H. Moon. (*J. Agric. Res.*, 1933, 47, 705–717.)—The fruit of the egg plant (*Solanum melongea*) is always eaten in the immature state. A study of the composition of the fruit from some 10 varieties of egg plant at different stages of maturity showed that the total solids generally ranged from 7 to 9 per cent. of the fresh green weight, and were highest at the time of flowering; decreased until the fruits were 15 to 20 days old, and, after that, changed little. Moisture-content was high. Total sugars (2·0 to 3·5 per cent. of the fresh fruit) varied little, but appeared to be highest in fruit 40 days old; total nitrogen was low, but a small amount of nitrate nitrogen was present at all stages except the very earliest. The sp.gr. of the fruit flesh was low (0·560–0·776), and the difference between that of the intact tissues and the expressed juice indicated the presence of 25 to 44 per cent. by volume of air in the tissues. Titratable acidity (as citric acid) was consistently low (0·1 to 0·2 per cent. at 15 days); total astringency (determined by a modification of the Procter–Loewenthal method) ranged from 0·15 to 0·35 per cent., and was highest at the time of flowering, thereafter continually decreasing. The failure of the material to retain its form during cooking is ascribed to the high moisture content associated with a change of much of the protopectin to pectin, and expulsion of air. Darkening on cooking appeared to be due to tannin-like substances and low acidity. When canned, the material turned dark, became soft and lost its form, possibly owing to the presence of oxygen and nitrates. The following results are typical of those obtained:

Variety	Age in days	Soluble solids Per Cent.	Insol. solids Per Cent.	Total solids Per Cent.	Reducing sugars Per Cent.	Sucrose Per Cent.	Total sugars Per Cent.	Titratable acidity Per Cent.	Total astringency Per Cent.	Substances hydrolysable by acid Per Cent.	Nitrate nitrogen Per Cent.	Total nitrogen Per Cent.
Florida Highbush	15	4·13	4·76	8·89	1·50	0·42	1·92	0·24	0·52	1·31	0·00014	0·26
New York Improved	15	3·78	4·58	8·36	0·96	0·40	1·36	0·27	0·47	0·92	0·00040	0·41
Black Beauty	15	3·73	4·72	8·45	0·99	0·45	1·44	0·26	0·43	1·04	0·00040	—
Chinese Giant	15	4·26	3·81	8·07	2·10	0·50	2·60	0·17	0·20	0·98	0·00078	—
Long Purple	20	4·06	4·06	8·12	2·01	0·69	2·70	0·21	0·12	1·16	0·00097	—
Japanese Long Purple	40	5·34	2·95	8·29	3·31	0·59	3·90	0·13	0·14	0·90	0·00095	0·72
Ovigerum	60	3·00	5·25	8·25	1·17	0·28	1·45	0·30	0·12	1·31	0·00115	—

D. G. H.

Determination of Iron in Beer by means of $\alpha\alpha'$-Dipyridyl. G. Bode. (*Woch. Brau.*, 1933, **50**, 321–323; *J. Inst. Brewing*, 1933, **39**, 658–659.)—Since direct qualitative tests for iron in beer with potassium thiocyanate are unreliable, and since quantitative determinations on the ash are uncertain owing to the presence of phosphates, the author has modified Blau's reaction (*Monatsh. Chem.*, 1898, **19**, 647), in which an intense red, soluble complex cation, stable to acids and alkalis, is produced by the interaction of ferrous ions and $\alpha\alpha'$-dipyridyl ($C_{10}H_8N_2$) in an acid medium. A mixture of 1 ml. of the sample, 0·5 ml. of concentrated sulphuric acid and 1 ml. of perhydrol is boiled gently until white fumes are evolved, more perhydrol being then added until all colour is destroyed. The iron is then reduced by addition of 0·5 ml. of a solution of sodium sulphite containing a slight excess of sulphur dioxide, and heating is renewed until white fumes again appear. One or two drops of a 1 per cent. solution of *p*-nitrophenol in alcohol are then added to the cooled liquid, followed by ammonia in very slight excess of the amount required for neutralisation, and 0·005 *N* sulphuric acid to neutralise this excess, as shown by the disappearance of the yellow colour. The mixture is then washed into a 10-ml. cylinder with three 2-ml. portions of the 0·005 *N* acid, the final volume being made up to 8·5 ml. with the acid. The resulting solution is mixed well with 0·5 ml. of the sodium sulphite solution and 1 ml. of a 0·5 per cent. solution of $\alpha\alpha'$-dipyridyl, and, when the colour is no longer increasing, its intensity is matched against the colours produced by addition, to 8·5 ml. of the acid containing the equivalent of 0·001 to 0·021 mgrm. of iron, of 0·5 ml. of sodium sulphite solution and 1 ml. of reagent. The standards are stable for some months in filled sealed test-tubes; allowance should be made for any blank on the reagents. Beer normally contains about 1 mgrm. of iron per litre, but 13 mgrms. per litre were found in a sample which developed iron-protein cloudiness; this was traced to imperfect removal of iron during the purification process. When 19 sq.cm. of sheet iron were suspended in 330 ml. of beer, the iron-content rose from 1 mgrm. per litre to 11, 40 and 135 mgrms. per litre after 3, 40 and 144 hours, respectively. J. G.

Distinction of Wine Vinegar from other Vinegars. J. Pritzker. (*Chem.-Ztg.*, 1933, 57, 927.)—The work of A. Patzauer (ANALYST, 1933, 58, 700) is criticised. In using Bonnstadt's *l*-tartaric acid method for the detection of tartaric acid the author shakes 10 ml. of vinegar with 1 ml. of a 20 per cent. solution of calcium acetate (not potassium acetate as erroneously given by Patzauer), then immediately adds 0·5 ml. of a 0·2 per cent. solution of *l*-tartaric acid, shakes again, and allows the mixture to stand for 12 hours. In the author's opinion there is no evidence that during the acetification of wine the tartaric acid present undergoes any change. It has also to be borne in mind that diseased and defective wines are converted into wine vinegar, and that in some of these the tartaric acid may be completely decomposed by bacteria. Tests on 5 genuine wine-vinegars gave only crystals of calcium tartrate, not the S-shaped crystals (more accurately termed propeller-shaped) described by Patzauer. These are obtained only in very dilute solutions of tartaric acid, and their formation bears no relation to the degree of acetic fermentation. Thus, *e.g.*, the "S" type was obtained with 0·002 to 0·04 per cent. of pure *d*-tartaric acid, but the crystals appeared longer and thicker with 0·06 per cent.; with 0·08 to 0·14 per cent. they became fewer in number. From solutions of 0·08 per cent. upwards calcium tartrate began to appear in increasing quantities, and with 0·2 per cent. no "S" crystals were to be seen. It is concluded that when the concentration of tartaric acid is less than 0·07 per cent. the calcium salts of *d*- and *l*-tartaric acids and the S-shaped crystals of racemic acid are all produced, but that the last only is insoluble. J. G.

Soya Bean Lecithin. F. Rothéa and F. Nielloux. (*J. Pharm. Chim.*, 1933, 125, 443–445.)—Soya bean lecithin may be added to chocolate mass in small quantities (some 0·3 grm. per cent.) to facilitate working and milling. The crude commercial lecithin is of a brownish-yellow colour, and a yellow oily layer separates on standing. The material is soluble in chloroform and ether, and partly soluble in acetone; the insoluble part consists of true lecithin, which may be separated from mineral matter by dissolving in chloroform the residue insoluble in acetone, filtering, and evaporating the chloroform. The lecithin may also be obtained by dissolving the chocolate mass in chloroform to eliminate the mineral matter, and precipitating it with at least 5 times its volume of acetone. As obtained by the first method the lecithin consists of a soft, orange-brown, gummy, elastic and translucent substance, which is greasy to the touch, and has a slight odour. The lecithin separated by the second method is in small granules, which gradually assume the gummy translucent state. This lecithin, although very soluble in chloroform and ether, differs from animal lecithin in being practically insoluble in ethyl alcohol. A specimen of the purified lecithin contained 2·76 per cent. of total phosphorus and 1·37 per cent. of total nitrogen, giving a ratio of P/N of 2·015, as compared with 2·07 for egg lecithin. If a weighed quantity of chocolate is extracted with chloroform or ether, the solvent evaporated, and the residue taken up with acetone, the lecithin will be left, and its percentage may be determined. D. G. H.

Comparative Action of Periodic Acid on α- and β-Glycerophosphoric Acids. New Method of Determining α-Glycerophosphates. P. Fleury and R. Paris. (*J. Pharm. Chim.*, 1933, **125**, 470–481.)—In agreement with the earlier observation that only those polyhydroxy compounds with an α-glycol function are attacked by periodic acid, it is found that this acid acts on α-glycerophosphoric acid, but not on its β-isomeride. For each molecule of the α-acid this reaction consumes one atom of oxygen, the molecule being split into one molecule of formaldehyde and one molecule of a compound which exhibits the properties of a phosphoric ether of glycollaldehyde. The reaction allows of the determination of α-glycerophosphoric acid in presence of the β-acid, the amount of periodic acid used up being readily determinable. Details of the procedure are given.

T. H. P.

Colour Reaction for Glycerin. K. Täufel and H. Thaler. (*Z. anal. Chem.*, 1933, **95**, 235–239.)—Glycerin in small amount (100γ or, in some instances, 50γ) may be detected by oxidising it to acraldehyde and oxidising this further to epihydrin aldehyde, which gives a red coloration with phloroglucinol. A few ml. (0·5 to 2 for wine, 2 to 5 for fruit wine, 5 to 10 for fermentation vinegar) of the liquid to be tested are evaporated to dryness in a porcelain dish on a water-bath, and the residue is mixed with 2 grms. of 40 per cent. lime paste and again evaporated to dryness; substances like tooth-paste, fats, etc., are treated at once with the lime paste. The dry residue is moistened with water and again evaporated, this operation being repeated. The dry mass, preferably after being moistened with absolute alcohol, is powdered with the help of a glass rod and then extracted with three quantities (3 to 4 ml. each) of absolute alcohol, the total extract being evaporated to dryness on a water-bath. The very small residue is taken up in 3 ml. of an absolute alcohol-ether mixture (1:1) and the solution is filtered, 3 ml. of the same mixture being used for washing. The filtrate is evaporated in a small distilling tube closed by a rubber stopper covered with tinfoil and having the condenser jacket fitted directly on the side-tube. The residue, after addition of a little pumice powder and 15 drops of glacial phosphoric acid, is carefully heated by fanning it with a small flame; the distillation is continued until boiling almost ceases. The cooled distillate, collected in a small test-tube (100 × 13 mm.), is treated with one drop of 3 per cent. hydrogen peroxide solution, and 1 ml. of concentrated hydrochloric acid, cooled under the tap, and shaken vigorously for a minute; 1 drop of 10 per cent. potassium iodide solution is added to destroy the excess of the peroxide and just sufficient 10 per cent. sodium thiosulphate solution to react with the separated iodine. The solution thus obtained is shaken with 0·5 ml. of a 0·15 per cent. solution of phloroglucinol in ether. Within

30 minutes a red to violet-red coloration appears in presence of epihydrin aldehyde. Occasionally the reaction mixture turns yellow, observation of the red colour thus becoming difficult; in such case the liquid is diluted with a little water, which destroys the yellow colour and at the same time dissolves any separated sodium chloride. Sucrose, which readily yields methoxyfurfuraldehyde, interferes with the test, and must be inverted. To this end, the initial residue in the porcelain dish is heated for 10 minutes on a boiling water-bath with about 5 ml. of 4 per cent sulphuric acid, the water being replaced meanwhile. Three grms. of the 40 per cent. lime paste are then added and the test is completed as described above.

From 2 to 3 mgrms. of glycerin are readily detectable when mixed with glucose, lactose, maltose, sucrose, starch, glycol, mannitol or hens' egg albumin, these substances alone giving no red colour when subjected to the above procedure. The method is applicable also to fats, fatty acids, and therapeutic and cosmetic preparations. Sweet apple juice is found to be free from glycerin, fruit wines contain appreciably less than grape wines, and vinegars of different origins are distinguished by different glycerin-contents. Blood and other body fluids are under examination. T. H. P.

Determination of the Smouldering Capacity of Tobacco. V. L. Nagy. (*Chem.-Ztg.*, 1933, **57**, 971–972.)—The use of powdered tobacco, rather than leaf or cut tobacco, is recommended for this test, and a device is described for measuring the speed of smouldering and the length of the layer of powder which burns.

T. H. P.

Biochemical

Nutritive Value of Pure Fatty Acid Esters. N. M. Cox, Jr. (*J. Biol. Chem.*, 1933, **103**, 777–790.)—The author has fractionated a natural fat (coconut oil) and has studied its various components by feeding experiments upon rats of the Wisconsin inbred strain. A brief summary is given of previously reported results of investigations of certain fatty glycerides; it is evident that the previous workers have used different species of experimental animals receiving diets of varying composition, and that relatively small amounts of the purified fat constituent were given. Feeding experiments have now been carried out on white rats with esters fractionated from coconut oil, and the series of saturated even-carbon fatty acids between 2 and 18 carbon atoms has been studied. It is shown that in the rat mixed ethyl esters permit of practically as good growth as do mixed triglycerides. The fat is well split, in contrast to the findings of others on dogs. When individual saturated fatty acid esters supply 77 per cent. of the caloric intake, nutrition, as measured by growth, *is in no case equal* to that obtained with mixtures of esters. Three portions of the saturated series resulted in death. Death occurred when ethyl butyrate and ethyl caproate were included in the diet because the animals usually refused to eat them. Ethyl palmitate and ethyl stearate did not support life because of inadequate absorption. With ethyl caprate, but more regularly with ethyl laurate, the rats died suddenly within 2 weeks. The toxicity is a function of the weight of the animal and of the level at which the fat is given. No characteristic chemical, bacteriological, or pathological changes were demonstrable. It is shown that saturated fatty acids with chains shorter than 10 carbon atoms, when given to rats, fail to appear to any conspicuous extent in the body-fat of the animal, in contrast with the longer-chain acids, which appear regularly. P. H. P.

Metabolism of Azelaic Acid. H. G. Smith. (*J. Biol. Chem.*, 1933, **103**, 531–535.)—Azelaic acid, a dibasic acid formed by *in vitro* oxidation of most naturally occurring unsaturated fatty acids, was given to dogs in amounts smaller than would be produced normally in the body if oxidation took place at the unsaturated linkages. The experiments described show that the acid was but little utilised by the animals; an average of 60 per cent. of the ingested acid was recovered from the urine. The acid was not excreted in the faeces. The accumulating evidence thus seems to indicate that the metabolic oxidation of fatty acids proceeds in a manner independent of the presence or position of a double bond. P. H. P.

Stability of Carotene in Ethyl Esters of Fatty Acids, and in Liver and Vegetable Oils. F. G. McDonald. (*J. Biol. Chem.*, 1933, **103**, 455–460.)—Two years ago it was recommended that carotene should be adopted as the provisional standard for vitamin *A*. In the preparation of carotene solutions for administration to animals, the solvent used is important because of the unstable character of carotene. A study of the stability of carotene in various solvents and under different conditions was suggested by this instability. The following solvents were selected: three highly-purified esters (ethyl butyrate, ethyl laurate and ethyl palmitate), one liver oil (medicinal cod-liver oil), and three refined vegetable oils [maize oil, arachis oil and Wesson (cottonseed) oil]. Solutions of 0·05 per cent. of carotene in these solvents were prepared by warming the mixtures to about 30° C. for a few minutes, and were stored in partly filled, tightly-stoppered brown bottles at 37° C., 24° C. and 5° C. Similar solutions were made up in tubes, which were evacuated, sealed and stored at 37° C. The carotene used was a mixture of the α- and β-isomers which melted at about 172° C. At the end of 1, 2, 4 and 8 weeks the solutions were sampled for carotene determinations, care being taken to avoid excessive exposure. The determinations were carried out with the aid of a spectrograph and sector photometer by suitably diluting the solutions in benzene and making a series of sector photometer spectrograms. From the observed extinction limits of the $462m\mu$ carotene absorption band the quantity of carotene was calculated. From the results, shown graphically, it is seen that solutions of carotene in ethyl butyrate, ethyl laurate, ethyl palmitate and arachis oil stored in partly filled, tightly-stoppered brown bottles at 37° C., 24° C. and 5° C., and in evacuated sealed tubes at 37° C. decomposed very rapidly. The loss of carotene in cod-liver oil under similar conditions was also rapid at 37° C. and 24° C., but it was considerably retarded at 5° C. and, in the absence of oxygen, at 37° C. Solutions in maize oil and Wesson oil in stoppered bottles at 37° C. and 24° C. were unstable, but at 5° C. they kept well for 4 weeks, and showed a small loss in 8 weeks. In evacuated sealed tubes at 37° C. they showed a loss of carotene of 15 per cent. in 8 weeks. Therefore, solutions of known concentration can be made up in maize oil and Wesson oil, stored in bottles at 5° C., and can be kept for as long as 4 weeks. It is evident that a combination of the favourable factors—absence of oxygen, low temperature, and the proper vegetable oil—constitutes the ideal condition for the storage of carotene solutions. P. H. P.

Micro-organisms and the Synthesis of Carotene and Vitamin *A*. C. A. Baumann, H. Steenbock, M. A. Ingraham and E. B. Fred. (*J. Biol. Chem.*, **1933, 103, 339–351.**)—Skinner and Gunderson (*J. Biol. Chem.*, 1932, **97**, 53) showed that a certain yellow *Corynebacterium* could synthesise a substance active in vitamin *A* from an inactive substrate, but did not determine whether vitamin *A* itself, its precursor carotene, or some other substance capable of functioning as vitamin *A* in the rat was produced. As vitamin *A* itself has not been found except in materials of animal origin, the authors have further examined this *Corynebacterium* to determine the nature of the biologically active material; they have also analysed cultures of other yellow organisms for carotene, and have made confirmatory tests by feeding rats which showed symptoms of vitamin *A* deficiency with the dried crude cultures of four different strains of these organisms. The results show that certain micro-organisms can synthesise carotene. Whenever an organism showed vitamin *A* activity, as determined by feeding experiments, enough carotene was found to be present to account for that activity. The vitamin *A* activity of micro-organisms did not appear to be affected by the presence of yellow pigments other than carotene. Since spectrographic determination failed to reveal an absorption band at $328m\mu$, it is exceedingly improbable that vitamin *A* as such is generally present in bacteria. Attempts to effect the transformation of carotene into vitamin *A* by micro-organisms failed; the organisms used included various bacteria, yeasts, moulds, and mixed cultures from soil, manure, air, water, milk, sewage, and peat. If the evidence is accepted that carotene is actually synthesised by the organisms in question, then in this respect these organisms resemble plants more closely than animals, since carotene, when present in animals, is of exogenous origin. The absence of vitamin *A* from micro-organisms and their failure to transform carotene into vitamin *A* likewise associate these organisms with plants, since vitamin *A*, as such, has not been demonstrated in a plant material. The similarity in structure of the carotene and the phytol molecules, as well as the fact that carotene always accompanies chlorophyll in plants, has led to the belief that carotene synthesis is in some way associated with chlorophyll activity. Micro-organisms, however, illustrate the fact that the formation of carotene is not dependent upon the presence of chlorophyll.

P. H. P.

Vitamin *A* Content of Barley. E. H. Hughes. (*J. Agric. Res.*, **1933, 47, 487–494.**)—The vitamin *A* content of California barley was determined and compared with that of yellow maize and white maize by measuring the increase of body weight in rats and noting external evidence; by observations of the effect on the oestrous cycle of the rat, assuming the truth of the conclusion of Evans and Bishop (*Anat. Rec.*, 1922, 17–18), that the constant appearance of cornified cells in the vaginal smear is a characteristic test for deficiency of vitamin in the diet; and by the quantitative method of Smith (*J. Agric. Res.*, 1930, 1147). Barley was found to be low in vitamin *A* content, and as the only source of vitamin *A* it did not produce normal growth in rats; in the sexually immature rat addition of vitamin *A* to a barley diet resulted in a decided increase in growth and a normal oestrous cycle. All the experiments showed that barley contains less vitamin *A* than yellow maize, and more than white maize. The amount appears to be less than one-sixth the amount in yellow maize. D. G. H.

Vitamin *A* Content of Pimiento Pepper. L. Ascham. (*Georgia Experiment Station Bull.*, No. 177, 1933.)—Pimiento pepper has been found to be rich in vitamin *A*, 2 mgrms. of dried pod giving a growth response in rats above that of the Sherman unit (*cf.* ANALYST, 1931, **56**, 492). The pepper contained 0·33 grm. of carotene per kilo. of dried material, as determined by the method of Zechmeister and von Cholnoky (*Ann. Chim.*, 1927, **70**, 455). It is computed that "a unit" of carotene, as determined by the results of pepper feeding, may conceivably be as low as, if not lower than, 0·0005 mgrm. D. G. H.

Losses of Vitamin *A* on Drying Fresh Raw Carrots, Sweet Potatoes and Canned Spinach. G. S. Fraps and R. Treichler. (*J. Agric. Res.*, 1933, **47**, 539–541.)—The loss in vitamin *A* on drying raw carrots, spinach, and sweet potatoes was determined, and the units of vitamin *A* were estimated by the Sherman and Munsell unit method. Raw yellow carrots contained approximately 43 units of vitamin *A* per grm. of fresh material or 377 units per grm. of dry material. Vacuum-dried carrots contained 77 units per grm., the carrots losing 80 per cent. of vitamin *A* when dried. Similarly, canned spinach after vacuum-drying lost 65 per cent. of its vitamin *A* (952 units per grm. of dry material being reduced to 333 units) and yellow Puerto Rico sweet potatoes lost 29 per cent. (70 units per grm. of dry material falling to 50 units). Fresh green vegetables may contain much higher amounts of vitamin than might be expected from experiments with the dried material. D. G. H.

Distribution of Vitamin *C* in Plant and Animal Tissues, and its Determination. O. A. Bessey and C. G. King. (*J. Biol. Chem.*, 1933, **103**, 687–698.)—The use of 2·6-dichlorophenol-indophenol has been found relatively satisfactory for the direct titration of vitamin *C* in animal and plant tissues. The authors describe various minor deviations from the method proposed by Tillmans (ANALYST, 1932, **57**, 260, 397). The titration of lemon juice with the dye and then with standard iodine solution has proved a rapid and satisfactory procedure for standardisation of the dye indicator, 2, 6-dichlorophenolindophenol. Acetic acid (8 per cent.) has been found preferable as an extracting and titrating medium with most plant tissues, whilst trichloroacetic acid (8 per cent.) is preferable with most animal tissues. Cysteine, glucic acid and heated sugar solutions may interfere seriously if present; glutathione and various other substances may interfere unless special precautions are taken. In interpreting the results it is necessary to take into consideration possible animal assays and the effect of interfering substances. Tables show comparisons of animal assays with dye titrations, and the amounts of vitamin *C* found in tissues of various animals. The adrenals and corpus luteum contain nearly the same amount of vitamin *C* (approximately 1·4 to 2·3 mgrms. per grm.); the brain, liver, testes, ovaries, and other glandular tissues comprise a second group, with considerably lower range (approximately 0·1 to 0·4 mgrm. per grm.); the more active muscular tissues, such as the heart, comprise an intermediate group (*e.g.* 0·05 to 0·15 mgrm. per grm.), whilst lean muscle contains only about 0·04 mgrm. per grm. There is a close relationship with the complex lipid content of animal tissues and also with the general rate of metabolism or respiration in the individual tissues. In younger animals the vitamin *C* content of the tissues tends to be higher than in older animals. In human tissues the distribution of vitamin *C* is similar to that in experimental animals. For those animals that require a direct dietary source of vitamin *C* the time required for marked general tissue depletion is apparently much shorter than the time required for symptoms of scurvy to appear. P. H. P.

Bacteriological

Reddening of Salted Hides. L. S. Stuart, R. W. Frey and L. H. James. (*U.S. Dept. of Agric., Tech. Bull.* No. 383, 1933.)—"Red heat" in salted hides is associated with the type of curing salt used. Red chromogenic organisms have been found in 34 out of 35 samples of crude solar-evaporated salts, and in 25 out of 39 open-pan evaporated granular salts. All the kiln-dried solar-evaporated salts (12 samples), all the vacuum salts (17 samples), and all the rock salts (62 samples) were found to be free from these organisms. The culture medium was a modification of Clayton Gibbs fish-salt-rice medium, in which the fish broth was replaced by hide broth. Growth could also be induced by inoculating salted calf skin and incubating at temperatures from 20° to 55° C. Chromogenic growths on salted hides are usually of a highly mixed flora, but by employing a large number of dilutions on dextrose agar, apparently pure cultures of red organisms can be obtained, and these under specified conditions will produce a reddening of the flesh of salted hides and skins. Repeated propagation on media of high salt-content markedly increases the salt tolerance of the organisms. They are identified provisionally as belonging to the *Thiobacteriales* or the *Myxobacteriales*. A very complete bibliography is appended, and is fully reviewed in the text. R. F. I.

Mould-growth Test for Minute Amounts of Arsenic. H. R. Smith and E. J. Cameron. (*Ind. Eng. Chem., Anal. Ed.*, 1933, 5, 400–401.)—The authors have utilised, as a test for arsenic, the property of certain mould growths of liberating arsenic as a gas with a garlic-like odour, found by Challenger and his co-workers to be trimethylarsine (ANALYST, 1933, 58, 235; *J. Chem. Soc.*, 1933, 95). It is claimed that 1 part per million of arsenic may be readily detected in a sample of 1 grm. or less. The mould *Scopulariopsis brevicaulis* (*Sacc.*) *Bainier*, as described in detail by Thom (*The Penicillia*, 1930), was used, with Czapek's* mixture as the medium for spore-growth. The following method was adopted:—A thin layer of melted Czapek's medium is placed in a Petri dish under sterile conditions, allowed to harden, and inoculated with 3 or 4 drops of aqueous spore suspension, which are made to cover the surface of the medium as completely as possible, and the whole is incubated for 48 to 72 hours at 30° C. until an obviously active growth develops. The sample (see below), about 1 grm., is distributed over the surface of the mould growth; the dish is covered and is allowed to remain at room temperature, and is tested for the characteristic odour by gently lifting the cover and smelling after periods of one-half, 1, 2 and 5 hours. If small amounts of arsenic (10^{-6} grm.) are present, the odour should be apparent in 2 to 5 hours, and sooner with larger amounts. The sample, if solid, should preferably be dry and ground to a coarse powder; if it is very fine, *e.g.* flour, it should be mixed with sodium carbonate, completely charred, and an extract of the residue in dilute hydrochloric acid used for the test; strongly smelling samples should likewise be charred and the extract used; oily constituents should be removed by previous extraction with a solvent. Liquid samples should first be rendered very slightly acid to litmus, and concentrated by evaporation, if necessary. Appreciable amounts of antimony do not interfere, but inorganic mercury compounds inhibit the test. Selenium and tellurium give odours similar to that of arsenic. S. G. C.

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* Czapek's medium contains 1000 ml. of water, 3 grms. of sodium nitrate, 1 grm. of potassium monohydrogen phosphate, 0·5 grm. of magnesium sulphate, 0·5 grm. of potassium chloride, 30 grms. of sucrose, and 15 grms. of agar-agar.

Toxicological and Forensic

Silicosis. W. R. Jones. (*J. Chem. Met. and Mining Soc., S. Africa,* 1933, **34**, 99–123.)—The author has previously described (*J. Hyg.*, 1933, **33**, No. 3) a technique for the examination of silicotic lungs, whereby the dust is left in a form in which it can be analysed chemically. For examination under the petrological microscope the dust is mounted in Canada balsam in the usual way. In all the residues of silicotic lungs examined there were countless mineral fibres, which, from their form, cleavage, sp.gr., birefringence and optical orientation, were identified as fibres of sericite. Most of the acicular, flexible fibres in lung residues range from 0·5 to 2μ in length, and from 0·1 to 0·5μ in thickness; many of them are bent towards their sharper ends.

Sericite, also known as "secondary white mica," is a hydrated silicate of aluminium and potassium. A specially pure specimen contained: silica, 46·58; alumina, 37·46; ferric oxide, 0·80; magnesia, 1·16; potash, 6·38; soda, 0·64; and water, above 110° C., 6·06; below 110° C., 0·30 per cent. (Shannon, *U.S.A. Nat. Mus. Bull.*, No. 131, p. 372). Certain minerals, notably potash felspars, under certain conditions of pressure, temperature, etc., become "sericitised," *i.e.* changed into minute scales and aggregates of acicular fibres of sericite. These fibres are held only loosely in the body of the rock, so that during the impact of drilling or blasting they are readily disseminated into the surrounding atmosphere. Sericite is most common in rocks that contain a high percentage of free silica in the form of quartz; it is not present, however, in all rocks that contain quartz. It is the dust from those rocks which contain much sericite that has been proved to cause silicosis. The dust from rocks containing little, if any, sericite, but containing a very high percentage of quartz, higher even than in rocks that have proved dangerous, has never given rise to a single authenticated case of silicosis.

Analyses of Mineral Residues from Silicotic Lungs.—Complete chemical analyses of three mineral residues were made by A. W. Groves at the Imperial College of Science and Technology, with the following percentage results:

Mineral residue from	SiO_2	Al_2O_3	Fe_2O_3	FeO	CaO	MgO	K_2O	Na_2O	TiO_2	P_2O_5	MnO	Water: Below 110°C.	Water: 110°C. to 350°	Water: Above 350°	Total
Lung A	49·52	21·99	3·55	—	—	1·73	2·47	0·78	0·08	2·55	—	2·18	0·51	0·33	97·49
Lung B	62·16	19·85	—	0·19	0·90	0·84	3·83	0·52	0·64	5·77	0·01	10·37	0·20	0·26	100·11
Lung C	59·23	26·38	—	0·11	0·45	0·62	0·78	0·64	0·78	2·68	0·01	2·27	1·39	0·56	99·57

Lung A was that of a man, 66 years of age, who had been engaged in the pottery industry for 50 years as earthenware hollow-ware jigger. Certified silicosis.

Lung B was that of an underground colliery worker, Swansea district, employed as a hard-heading worker. Certified silico-tuberculosis.

Lung C was that of a collier at Pontycymmer, S. Wales, aged 51 years, who had also worked as a quarryman in N. Wales. Certified silico-tuberculosis.

Under the petrological microscope these three residues were found to consist mainly of minute acicular fibres of sericite, but in the potter's lung there was also a little clay. Some of the alumina in this residue should, therefore, be allocated to kaolin (SiO_2, 43·5; alumina, 36·9; water, 19·6 per cent.), but, as the ratio of alumina to silica in kaolin is not appreciably different from the ratio in sericite, any correction would influence the results only to a minor extent. The presence of this aluminium silicate explains, however, the lower potash-content in relation to alumina in A than in B and C. The water determinations proved that the fibrous mineral was not one of certain mineral constituents of clay that lose all their water at temperatures well below 350° C. If the alumina in these three residues is allocated to the amounts of silica, potash and water required to form sericite, the following results are obtained:

	A Per Cent.	B Per Cent.	C Per Cent.
Sericite ..	55·83	51·01	59·48
Free silica ..	22·04	37·35	19·66

It is important to note that the few large grains of quartz in these residues contribute their quota of free silica in the analyses out of all proportion to their probable silicotic effect in the lung. It is mainly the presence in the rocks of fibrous minerals, such as sericite, sillimanite, tremolite, etc. (or a fibrous form of free silica as in chert, or a fibrous rock as in pumice) in aggregates which are liberated during drilling, etc., into the atmosphere as individual fibres, that enables sufficient material in course of time to enter the lungs to cause silicosis. It is not contended that sufficient minute particles of quartz could not, under any conditions, enter the lungs to cause silicosis, although the cases investigated appear to show conclusively that they have not done so; but it is maintained that the fibrous minerals hasten the process so greatly that their presence in the exploited rocks and materials is of far greater importance than the presence of quartz in causing the disease. (*Cf.* ANALYST, 1933, **58**, 775.)

Spectro-photometric Study of Fluoro-Methaemoglobin for Detecting Methaemoglobin and for Determining Fluorides. R. Fabre and (Mlle) S. Bazille. (*J. Pharm. Chim.*, 1933, **125**, 465–470.)—In presence of a small quantity of sodium fluoride, acid methaemoglobin exhibits a spectrum composed of two bands—one very intense—in place of the four bands shown in absence of fluoride. By spectro-photometric examination of blood containing fluoride, it is possible to detect one part of methaemoglobin in the presence of about nine parts of haemoglobin. For the zone $\lambda = 6100$ to 6200 Å.U., the position of maximum absorption varies little with methaemoglobin solutions containing from 0·1 to 2 mgrms. of sodium fluoride per 10 ml., and within these limits of concentration it is possible, by measuring the optical density at the maximum absorption, to determine the fluoride-content with satisfactory accuracy. T. H. P.

Organic Chemistry

Indicator Properties of *p*-Nitrophenyl-acetyl-hydrazine, 2, 4-Dinitrophenyl-acetyl-hydrazine, and 2, 4, 6-Trinitrophenyl-acetyl-hydrazine. A. Bloom and A. Osol. (*Amer. J. Pharm.*, 1933, **105**, 551–553.)—The nitrophenyl-acetyl-hydrazines were prepared by acetylisation of the corresponding nitrophenyl hydrazines with an equivalent weight of acetic anhydride, glacial acetic acid being used as solvent, and the mixture boiled for several hours under a reflux condenser. The precipitated nitrophenyl-acetyl-hydrazines were filtered off and recrystallised from alcohol. The three products had the following melting points: (1) *p*-nitrophenyl-acetyl-hydrazine, 196·8° C.; (ii) 2, 4-dinitro-phenyl-acetyl-hydrazine, 209–210° C.; (iii) 2, 4, 6-trinitrophenyl-acetyl-hydrazine, 222–223° C. Their indicator properties were compared with those of methyl red. All three were satisfactory for the titration of strong acids, the acid colours in each case being pale green, and the alkaline (i) brown, (ii) reddish-brown, and (iii) orange-brown, respectively. These indicators are not suitable for the titration of alkaline solutions, since they gradually fade, and the colour-changes are indistinct.

D. G. H.

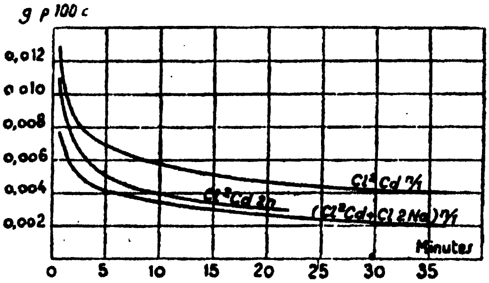
Determination of *o*-Toluidine. S. Ueno and H. Sekiguchi. (*J. Soc. Chem. Ind., Japan*, 1933, **36**, 613B.)—About 1 grm. of the *o*-toluidine is converted into the hydrochloride by adding 1 ml. of concentrated hydrochloric acid. After being well mixed a small portion is spread on a watch-glass and left overnight in a desiccator containing sulphuric acid, after which its m.pt. is determined.

The m.pts. of anhydrous *o*-toluidine hydrochloride in the absence and presence of the *p*- and *m*-isomers were as follows, and from these results the degree of purity of a sample may be deduced.

o-Toluidine Per Cent.	*p*-Toluidine Per Cent.	*m*-Toluidine Per Cent.	M.pt. of hydrochloride observed. °C.
100	—	—	216
98	2	—	213·8
96	4	—	211·6
94	6	—	209·7
92	8	—	207·4
90	10	—	205·4
98	—	2	213·8
96	2	2	211·9
96	—	4	212·1
94	4	2	210·0

Since the hydrochloride is very hygroscopic, it is recommended that in very rainy weather the m.pt. of the hydrobromide should be taken. R. F. I.

Determination of Pyridine in Dilute Aqueous Solution. V. Ionescu and H. Slusanchi. (*Bull. Soc. Chim.*, 1933, **53**, 1087–1096.)—The addition of cadmium chloride to sufficiently concentrated aqueous pyridine results in the formation of a crystalline precipitate of cadmium pyridine chloride. The corresponding reaction with mercuric chloride is more sensitive. The sensitiveness of both reactions increases with increased addition of cadmium or mercuric chloride, more particularly if sodium chloride is also present. Under specified conditions, as selected for the method below, relations have been found to exist between the time required for the appearance of the precipitate and the concentration of pyridine, when either *N* cadmium chloride-sodium chloride solution or *N* mercuric chloride-sodium chloride solution are employed as the reagent; the relations are shown as curves in the figure, in which the ordinates show the concentration of pyridine (grm. per 100 ml.) in the final solution *after* the addition of 50 per cent. by volume of reagent, and the abscissae show the time in minutes for the appearance of the precipitate. The method proposed for the determination of pyridine is as follows: To a sample of the solution contained in a test-tube is added 50 per cent. by volume of the reagent. The mouth of the test-tube is closed with the thumb, and it is inverted 2 or 3 times to mix the contents. The liquid is kept under observation with the aid of a lens, and the period of time up to the appearance of the first signs of the precipitation of acicular crystals is noted. This time, multiplied by 1·5, gives the time from which the corresponding concentration of pyridine can be read from the curves. The temperature of the solution should be 16 to 18° C. Some preliminary trials may be required to find the appropriate dilution of the sample solution to be used in the method, such that the time determined shall fall within the limits of the curves. The limits of sensitiveness of these reactions for pyridine are 3 parts in 10,000 parts with the cadmium reagent, and 0·45 part in 10,000 parts with the mercury reagent; the mercury reagent should thus be used for the weaker solutions of pyridine. S. G. C.



Determination of Sulphur in Benzene. H. A. J. Pieters, J. Van Iterson and S. J. H. Spronck. (*Chem. Weekblad*, 1933, **30**, 756–762.)—*Free Sulphur.*—Existing methods are reviewed. In that of the *Benzol Verband* (*ibid.*, 1933, **30**, 675) the benzene is evaporated, the residue is heated with sodium hydroxide solution and hydrogen peroxide, and the resulting sulphate is determined in the usual way. This is supposed to give "α-sulphur," which is held to be responsible for the corrosion of copper; actually, complete recovery of added sulphur (5 to 40 mgrms. per litre) was obtained. The copper stain-test (*cf.* Ormandy and Craven, *J. Inst. Pet. Tech.*, 1923, **9**; 1925, **11**) will detect over 5 mgrms. per litre, but is not quantitative, and the following method, adapted from that of E. Dittrich (*Brenstoff-chem.*, 1933, **14**, 282), gives results as accurate as the first method (for 1·7 to 25·3 mgrms. of sulphur per litre), but in much less time:—100 to 1000 ml. of the sample are shaken for 30 minutes with 2 ml. of pure mercury, and filtered, and the residue is washed first with pure benzene and then with a little warm water. The filter and its contents (sulphur as mercuric sulphide), together with 2 grms. of aluminium turnings, are placed in a distillation flask (a special apparatus is described), which is then closed, and the air is displaced by means of a stream of carbon dioxide. Concentrated hydrochloric acid (50 ml.) is then added through a funnel attached to the flask, a little at a time, and the gas evolved is washed first in 50 ml. of water and then in two wash-bottles, each containing 50 ml. of a mixture prepared by diluting a solution of 25 grms. of cadmium acetate in 200 ml. of glacial acetic acid to 1 litre; the second serves as a control. The flask is warmed towards the end of the reaction, which is complete after 20 to 30 minutes, and the contents of the cadmium acetate wash-bottles are then transferred to an Erlenmeyer flask and are mixed with 10 ml. of 0·1 *N* iodine solution and 5 ml. of 4 *N* hydrochloric acid. The flask is stoppered for 2 minutes, and the excess of iodine is then titrated with 0·05 *N* sodium thiosulphate solution. *Carbon disulphide.*—If this is less than 500 mgrms. per litre the golden-brown colour produced on mixing, in the order given, 1 ml. of sample, 1 ml. of a 1 per cent. solution of diethylamine in pure benzene, 1 ml. of a 0·03 per cent. solution of crystalline copper acetate in cold alcohol, and 7 ml. of alcohol, is matched within 20 minutes against the colour produced from standards containing 1 to 0·01 per cent. of carbon disulphide in pure benzene (*cf.* Callan, Henderson and Strafford, ANALYST, 1932, **57**, 590). For larger quantities, 20 to 100 ml. of sample are evaporated with 10 ml. of a solution prepared by dissolving potassium hydroxide in the minimum amount of water and subsequently diluting with 96 per cent. alcohol until the strength is 6 per cent., and filtering on the following day. The residue is warmed with 30 ml. of 3 per cent. hydrogen peroxide for 20 minutes, after which it is cooled, and the excess of alkali over the sulphuric acid so produced is back-titrated with 0·1 to 0·5 *N* sulphuric acid ($1H_2SO_4 \equiv \frac{1}{2}CS_2$) with bromphenol blue as indicator (*cf.* Hoffert and Claxton, *Motor Benzole*, 1931). *Thiophen* (after Schwalbe).—The blue colour produced from 1 ml. of sample and 25 ml. of a 0·05 per cent. solution of isatin in concentrated sulphuric acid is matched, using a series of standards containing from 1 to 0·01 grm. of thiophen per litre. *Total Sulphur.*—A modification of Davidson's procedure (*Gas. J.*, 1920, **185**, 95; Hoffert and Claxton, *loc. cit.*) is preferred to the B.E.S.A. (1921, No. 35) method. An apparatus is pictured and described in which the sample is diluted with 4 volumes of 96 per cent. alcohol and is fed by gravity, with sulphur-free air, into a special burner placed in the wide limb of a U-tube, the other limb being a measuring burette connected to it by means of a capillary tube. The lamp is enclosed, by means of a mercury-seal, in a chimney which forms the wide limb of the tube and conveys the products of combustion into wash bottles, where sulphur compounds are oxidised to sulphuric acid by means of 1·5 per cent. hydrogen peroxide neutralised with potassium hydroxide solution, the sulphuric acid being then precipitated or titrated.

J. G.

Chemistry of Australian Timbers. Part 3. Chemical Composition of Four Pale-Coloured Woods of the Genus *Eucalyptus*. W. E. Cohen, A. G. Charles and A. B. Jamieson. (*Commonwealth of Australia, Council of*

Sci. and Indust. Res., Pamphlet No. 44, Aug. 1933.)—The Table shows the average values for 4 woods of the Genus *Eucalyptus* ("Ash" group) as determined by the methods previously described (*cf.* Cohen and others, ANALYST, 1932, **57**, 101; 1933, **58**, 635, 636), and expressed as percentages on the wood dried at 105° C. These woods vary from white to pale brown in colour, and are of open texture, low density and moderate durability. They occur in the east of Australia and in Tasmania and are used for constructional work, furniture and pulping. Identification by physical characteristics is difficult; the principal chemical features are the relatively low ash and extractive contents, and high cellulose values. Except for *E. obliqua*, which contained variable amounts of extraneous matters, the values of all determinations for each species were uniform. Apart from certain chemical points of resemblance in the case of *E. gigantea*, there are few similarities between these woods and the North American hardwoods, the cellulose, ash and total pentosan contents in particular being lower in the former case; mesquite is excluded from the latter, since it resembles *E. obliqua*, although only in chemical composition. Distinction of *E. gigantea* and *E. regnans*, and in some cases of *E. obliqua*, is difficult by macroscopic and microscopic methods, but the ratios of solubility in $N/8$ sodium hydroxide solution to solubility in (*a*) hot water, (*b*) alcohol, and (*c*) in the mixture of benzene and alcohol, are useful diagnostic characters, maximum and minimum values being, respectively:—*E. gigantea*, (*a*) 6·3, 3·3; (*b*) 9·4, 3·2; (*c*) 12·7, 7·3. *E. obliqua*, (*a*) 2·7, 1·3; (*b*) 2·3, 1·4; (*c*) 6·2, 1·9; *E. regnans*, (*a*) 3·5, 1·3; (*b*) 11·5, 1·8; (*c*) 25·4, 3·6; *E. sieberiana*, (*a*) 6·6, 1·9; (*b*) 4·7, 1·6; (*c*) 5·7, 2·5. A diagrammatic scheme of chemical analysis has been evolved, the value of which, however, is limited by the facts that the samples of *E. gigantea* were all from one locality, and that there are no chemical values that can be used in all cases to separate definitely one species from all the others. J. G.

				Solubility in						Pentosans			
Species	Number of Samples	Ash	Alkalinity of ash (ml. of 0·1N H_2SO_4 per grm.)	Hot Water	Cold Water	Alcohol	Ether	$N/8$ Sodium hydroxide Sol.	Be Alcohol (2:1)	Total	Cellulosic	Lignin	Cellulose
		Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.
E. gigantea ..	6	0·06	0·09	4·0	1·9	4·3	1·1	16·9	1·5	20·8	10·9	19·9	56·9
E. obliqua ..	20	0·05	0·03	14·3	9·5	15·1	1·3	26·6	7·7	15·0	7·5	21·1	46·6
E. regnans ..	13	0·07	0·06	10·2	5·0	6·7	0·5	20·1	3·2	17·6	8·5	20·4	49·6
E. sieberiana ..	10	0·06	0·09	9·2	6·4	10·1	1·4	23·7	6·4	17·0	9·5	19·9	50·0

Inorganic Chemistry

Determination of Nitrogen by Combustion in the Electric Arc. W. D. Treadwell and T. Zürrer. (*Helv. Chim. Acta*, 1933, **16**, 1180–1187.)—Nitrogen in noble gases is determined either by absorption over lithium or by combustion with excess of oxygen, with the aid of an electric spark (Cavendish). The latter procedure is very slow, which is ascribed to lack of movement in the gas. The authors expedite the combustion by rapid circulation of the gases. The circuit includes a flask containing dilute caustic soda solution, the progress of the neutralisation of which by the nitric oxides is observed conductometrically. The decrease in conductivity is proportional to the nitrogen. The paper contains a description with illustrations of the apparatus and directions for its use. The speed of combustion of the nitrogen is given as 0·2 to 0·3 ml. per minute with an arc of about 20 watt. The last of the nitrogen combines at a lower speed (about 0·1 ml. per minute), the determination requiring 15 to 120 minutes according to quantity.

W. R. S.

Determination of Lead by means of Picrolonic Acid. F. Hecht, W. Reich-Rohrwig and H. Brantner. (*Z. anal. Chem.*, 1933, **95**, 152–163.)—The determination is analogous to that of calcium with the same reagent (ANALYST, 1931, **56**, 832). The lead precipitate forms pale greenish-yellow crystals of the composition $Pb(C_{10}H_7N_4O_5)_2.1{\cdot}5H_2O$ (Pb factor, 0·2725). The solubility of the compound is equivalent to 6·61 mgrms. of lead per litre. The neutral nitrate solution, as free as possible from alkali and ammonium salts, and containing 0·1 grm. of lead in about 50 ml., is heated to incipient boiling, and precipitated, drop by drop, during agitation, with the required quantity of the reagent (100 ml.), *i.e.* a 0·01 *N* solution containing 2·64 grms. per litre. A further addition of half the quantity of reagent previously used is then made all at once. The liquid is cooled in an ice-chest, filtered through a porous crucible, and the precipitate is washed with a minimum of ice-cold water until the washings are colourless. Constancy of weight is reached by drying at 130 to 140° C. for 1 to 1½ hours. The procedure was also found suitable for micro-work, the technique for which is described.

W. R. S.

Use of Amyl Alcohol in the Sodium Diethyl Dithiocarbamate Method for the Determination of Copper. R. W. Thatcher. (*J. Amer. Chem. Soc.*, 1933, **55**, 4524.)—A difficulty is sometimes found in securing a sharp separation of the amyl alcohol layer in the MacFarlane method for determining the presence of copper in organic tissues (*J. Biol. Chem.*, 1932, **26**, 1022). The difficulty may be overcome by the use of isoamyl alcohol instead of normal amyl alcohol. This difference in behaviour is possibly due to the lesser solubility in water of the iso compound.

R. F. I.

Osmium Tetroxide as Catalyst for the Oxidation of Arsenious Acid. K. Gleu. (*Z. anal. Chem.*, 1933, **95**, 305–310.)—In 0·5 *N* sulphuric acid solution, the oxidation of arsenious acid by means of permanganate or ceric sulphate proceeds stoichiometrically after addition of 3 drops of a 0·01 *m* solution of osmium tetroxide in 0·1 *N* sulphuric acid (bulk, 100 to 200 ml.). The oxidation proceeds quite smoothly to a sharp end-point, provided that the titration is not hurried. Ceric sulphate, which has no action on arsenious acid in sulphuric acid solution, acts at once in presence of a little osmium tetroxide. The indication of the end-point is given by ferro-*o*-phenantrolin, which is decolorised by oxidation after complete oxidation of the arsenious acid.

W. R. S.

Separation of Zinc from Aluminium. J. N. Frers. (*Z. anal. Chem.*, 1933, **95**, 1–36, 113–142.)—The paper contains a detailed examination of the subject and an investigation of the method adopted, *viz.* precipitation of zinc sulphide from feebly acid solution. The procedure is as follows: The solution of 0·2 grm. Zn (or less) [containing not more chloride than is equivalent to the (Al+Zn), otherwise evaporation with sulphuric acid is necessary] is treated with enough ammonium sulphate to provide a 4 per cent. solution after dilution to about 400 ml., and 20 drops of tropaeolin OO indicator, and is neutralised with pure ammonia until the tint matches that of the indicator in the washing liquor (4 per cent. ammonium sulphate) under the same conditions. After addition of filter pulp (half an 11-cm. paper) the solution is boiled and submitted, while cooling, to a vigorous current of hydrogen sulphide for ten minutes, then to a moderate current for half an hour. The precipitate is collected and washed with the hot wash-liquor saturated with hydrogen sulphide. The paper may be kept filled with distilled water in the funnel for an hour before use (method not stated); this prevents any cloudiness of filtrate. Filter and precipitate are ignited in a glazed porcelain crucible with liberal admission of air; the oxide is then treated for 10 minutes with a current of hydrogen sulphide while the bottom of the crucible is heated to incipient red heat. After cooling for 5 minutes in the gas stream, the crucible may be removed. The precipitate is weighed as ZnS. The aluminium in the filtrate from the zinc sulphide is determined in the usual manner by neutralisation with ammonia or by boiling with sodium thiosulphate. W. R. S.

Antimony as Indicator Electrode in the Potentiometric Titration of Iron and Aluminium. E. W. Kanning and F. H. Kratli. (*Ind. Eng. Chem., Anal. Ed.*, 1933, 5, 381–383.)—The titration of ferric and aluminium chlorides with sodium hydroxide solution has been followed potentiometrically, an antimony indicator electrode being employed and its potential being measured against a saturated calomel electrode. With ferric chloride solutions a jump in the potential occurred at the point of precipitation of ferric hydroxide; with aluminium chloride a jump at a higher value of potential occurred, corresponding with the precipitation of aluminium hydroxide, followed by a less distinct jump when the aluminium hydroxide re-dissolved, forming sodium aluminate. The potential jumps enabled the end-points to be located accurately with ferric and aluminium chlorides separately, but with mixtures the potential changes were less pronounced, and the "end-point" for the equivalence point of ferric hydroxide was too early, and that for aluminium hydroxide was too late, rendering the method only an approximate one. The titrations were less precise with 0·1 *N* than with *N* sodium hydroxide solution. The presence of alkali sulphate caused more or less considerable errors. The hydrogen electrode, owing to the slowness with which equilibrium values of potential were reached, was found less satisfactory than the antimony electrode in the above titrations. S. G. C.

Indirect Volumetric Determination of Chromium. A. Ionesco-Matiu and S. Herscovici. (*Bull. Soc. Chim.*, 1933, 53, 1032–1038.)—The process is an application of a general "mercurimetric" method, due to the authors, in which mercuric sulphate is titrated with sodium chloride in the presence of sodium nitroprusside, which acts as an indicator by forming a turbidity of mercuric nitroprusside which dissolves to a clear solution when sufficient chloride has been added to convert the mercury into mercuric chloride. The scheme adopted is to precipitate the chromium, which must be present as chromate, as mercurous chromate, and to dissolve this precipitate, after centrifuging and washing, in dilute sulphuric acid containing potassium permanganate, thus obtaining mercuric sulphate, which is titrated as indicated. An empirical relation between the mercury and the chromate has had to be worked out, since the composition of the mercurous chromate as precipitated lies between those of normal and basic mercurous chromate. For further details the original paper should be consulted.

S. G. C.

Determination of Alkalis as Silicofluorides. W. D. Treadwell and W. König. (*Helv. Chim. Acta,* 1933, **16**, 1201–1208.)—When alkali chloride, nitrate, or fluoride is evaporated with a sufficiency of hydrated silicic acid and excess of hydrofluoric acid, it is converted into pure silicofluoride, which can be heated until constant in weight. The solution is treated in a small platinum basin with 3 times the theoretical amount of silicic acid and 1 to 2 ml. of re-distilled 40 per cent. hydrofluoric acid per 0·1 grm. of added silica. The liquid is evaporated to dryness, and the residue is heated for 1 to 2 hours in an oven at 120° C., after which it can be weighed in the open basin. The silica is prepared from waterglass and hydrochloric acid, the jelly being repeatedly dissolved in pure caustic soda solution, and re-precipitated; after being freed from chloride by washing, it is dried on the water-bath. The alkali silicofluoride may also be titrated after solution in 10 ml. of water, addition of 10 to 25 ml. of strictly neutral 4 *N* calcium chloride solution, and short heating: $Na_2SiF_6+3CaCl_2+3H_2O=3CaF_2+H_2SiO_3+4HCl+2NaCl$. The liberated acid is titrated against bromcresol purple. Titration of the weighed mixed silicofluorides permits of the indirect determination of two alkalis. Very good results are obtained with lithia. The separation from magnesium is best effected by means of *o*-hydroxyquinoline (ANALYST, 1927, **52**, 431), especially if lithium is present; the filtrate containing the alkalis is evaporated to dryness, and the residue is cautiously ignited, and dissolved in hydrochloric acid, and the carbonaceous particles are filtered off. The filtrate is evaporated, and the residue is converted into silicofluoride as described above. W. R. S.

Determination of Small Quantities of Fluorine by the Steiger-Merwin Reaction. I. Optimum Conditions, and Interference. II. Details of Procedure. H. J. Wichmann and D. Dahle. (*J.A.O.A.C.*, 1933, **16**, 612–619, 619–624.)—The conditions governing the bleaching effect of the fluorine ion on the colour of a peroxidised titanium solution (*cf.* Steiger, ANALYST, 1908, **33**, 139; Merwin, *Amer. J. Sci.*, 1909, **28**, 119) have been investigated. This effect increases as the p_H value of the solution increases to 1·5, and subsequently decreases to practically zero at p_H about 2·5. Moreover, the bleaching action per unit of fluorine increases as the concentration of fluoride increases and as that of titanium diminishes, and, as far as a certain limit, it is proportional to the quantity of fluorine present. Interference with the effect is caused by a number of substances, including the colouring matter of fruit, phosphates, aluminium, iron, and sulphates.

The results of this investigation form the basis of the following procedure, which gives satisfactory results when applied to the determination of fluoride in apple peelings, cabbage, and rat feed containing known amounts of fluorides. The sample is ashed, and the ash is distilled at 135° C. with sulphuric or perchloric acid. Of the distillate, filtered if necessary, an aliquot part estimated to contain between 0·01 and 0·05 mgrm. of fluorine is placed in a Nessler tube, together with 1 ml. of titanium chloride solution (2 ml. of a 20 per cent. solution and 20 ml. of hydrochloric acid, made up to 1 litre), and 1·3 ml. of hydrochloric acid (1+9). The liquid is then made up nearly to the 50-ml. mark with water, 2 ml. of hydrogen peroxide solution (5 ml. of the 30 per cent. solution made up to 100 ml.) being added and the tube filled to 50 ml. and inverted to mix. The p_H value is determined and adjusted to 1·5 ± 0·02. Samples containing appreciable amounts of chloride or nitrate give distillates containing mineral acid, and experimental adjustment of the p_H is then necessary.

When the necessary amount of acid is ascertained, a second sample tube is prepared, the volume of hydrochloric acid added being adjusted as found necessary. This tube is compared with the standard tubes. These are made by adding, to six of the Nessler tubes, 1 ml. of the titanium reagent and sufficient of the dilute hydrochloric acid (about 1·3 ml.) to give the p_H value 1·5 ± 0·02. Next are added to the six tubes 0, 1, 2, 3, 4, and 5 ml., respectively, of sodium fluoride solution (containing 0·01 mgrm. of fluorine per ml.); 40 ml. of water are added to each, then 2 ml. of the peroxide solution, and sufficient water to make 50 ml. The tubes are inverted to mix, and the p_H value of each is determined to see that this is 1·5 ± 0·02 in all cases. If the colour of the sample tube does not fall within those of the 0·01 and 0·05 mgrm. standard tubes, another aliquot portion of the distillate must be used, and the amount of acid necessary to give the p_H value 1·5 determined anew. If the fluoride-content of the sample is very small, it may be necessary to concentrate the distillate from the ash—after making it distinctly alkaline—before proceding with the test. Four samples of Arizona drinking water showed from 0·45 to 3·92 parts of fluorine per million. Sprayed apples showed 2 parts; sprayed cabbage, 33·6 for the outside leaves, and 2·7 for the remainder of the head; sprayed celery (2 samples), 7·6 and 3·6 in the petioles, and 77·1 and 135·3 in the leaves. Strawberry juice, preserved with fluoride, gave 141 parts of fluorine per million.

T. H. P.

Volumetric Determination of Small Quantities of Iodine. J. F. Sadusk and E. G. Ball. (*Ind. Eng. Chem., Anal. Ed.*, 1933, 5, 386–389.)—Some factors affecting the sensitiveness and accuracy of the volumetric method which involves oxidation of iodine to iodate and subsequent titration with thiosulphate have been investigated, and the following modified method was developed:—To the neutral iodide solution (50 ml.), contained in a 125-ml. Erlenmeyer flask, are added 1 ml. of 2 *N* sulphuric acid and sufficient bromine to colour the liquid yellow; the bromine is added as vapour, obtained by passing air through liquid bromine contained in a gas-washing bottle, and delivered by a jet just above the surface of the iodide solution, which is swirled gently until sufficient bromine is absorbed. A few glass beads are placed in the flask, and the bromine is dispelled by boiling, which is prolonged for 2 minutes after the bromine colour has disappeared. The solution is cooled, water is added to replace that lost in the boiling; 1 ml. of potassium iodide solution (10 per cent.) is added, and the liberated iodine is titrated with standard thiosulphate solution, starch being used as indicator. Results accurate to within a few units per cent. of the total were obtained with amounts of iodine from

1 mgrm. down to 0·02 mgrm., 0·005 *N* thiosulphate solution being used for titrating the larger amounts and 0·001 *N* for the smaller amounts. Under the conditions employed, the smallest quantity of iodine required to give a blue colour with starch was found to vary with the temperature of the solution; thus at 31° C. the quantity was 0·024 mgrm., while at 17° C. it was 0·012 mgrm. The p_H value of the solution must be maintained between 1·0 and 2·0, since at higher p_H values the interaction of iodine and thiosulphate proceeds slowly, while at lower p_H values the rate of oxidation of iodide by air becomes marked, but it is slower the lower the temperature; solutions of potassium iodide at p_H 1–2 showed no appreciable oxidation by air in half-an-hour. The practice of some workers of adding phenol or salicylic acid to destroy any residual bromine after the oxidation process is not only unnecessary, but tends to cause low results; a small amount of salicylic acid used as a preservative for the starch indicator is, however, harmless. Iron was found to interfere when more than 0·1 mgrm. was present; bromide in small amount was without effect, but when present in larger amount, *e.g.* more than a 20-fold excess over the iodine present, it prevented quantitative oxidation of the iodine by bromine.

Determination of Iodine in "Iodised Salt."—A 5-grm. sample is dissolved in 100 ml. of water, neutralised to methyl orange indicator with sulphuric acid, and acidified with 2 ml. of 2 *N* sulphuric acid; the oxidation and subsequent titration are carried out as in the above method. S. G. C.

Direct Titration of Sulphate. W. C. Schroeder. (*Ind. Eng. Chem., Anal. Ed.*, 1933, **5**, 403–406.)—The titration of sulphate with barium chloride can be accomplished with the aid of tetrahydroxyquinone as internal indicator, which yields a red barium salt at the point of complete precipitation of the sulphate. Tetrahydroxyquinone may be prepared by treating glyoxal sodium bisulphite with sodium carbonate (Homolka, *Ber.*, 1921, **54**, 1393); it is unstable in solution, necessitating its being kept in solid form; it dissolves rapidly in water when finely powdered in intimate mixture with 400 parts of potassium chloride, thus providing a satisfactory method of introduction into the test solution.

Method.—The cold sulphate solution (25 ml.), containing between 2 and 20 mgrms. of sulphate, is rendered faintly acid to phenolphthalein with hydrochloric acid, and 25 ml. of alcohol are added; 0·2 grm. of the tetrahydroxyquinone-potassium chloride mixture is dissolved in the solution, giving it a deep yellow colour. To the solution is added barium chloride solution (0·025 *N*) at a steady rate, with constant shaking, until a brown colour begins to form. From this point, barium chloride solution is added 2 or 3 drops at a time, with shaking, until a red colour appears throughout the bulk of the solution, marking the end-point. A "blank" of 0·1 ml. of barium chloride solution, which is required to colour the indicator, is deducted from the total volume used; 1 ml. of 0·025 *N* barium chloride solution is equivalent to 1·2 mgrm. of SO_4. In test experiments, results within ±0·3 mgrm. were obtained with up to 20 mgrms. of sulphate, but above this amount the results were low. The maximum amounts of other ions which, it is stated, may be tolerated without causing error are: 7·5 mgrms. of carbonate, 5 mgrms. of aluminium, 25 mgrms. of silicate, and 15 mgrms. or more of magnesium. Calcium, up to the amount at which calcium sulphate is precipitated, is without effect, and chloride is without effect, but iron in amounts above 0·1 mgrm. interferes and must be removed. The whole subject of volumetric determination of sulphate is reviewed, and 120 references are cited. S. G. C.

Colorimetric Determination of Iodine by the Chloroform Method. K. L. Maljaroff and W. B. Matskiewitsch. (*Mikrochem.*, 1933, 13, 85–91.)—The effect of interfering salts on the colorimetric determination of iodine by the chloroform method has been investigated. Both the volume of the solution under examination and that of the chloroform must be the same in every test, and the volume of chloroform must not be too small, as the partition coefficient for iodine in water and chloroform is 135, so that when the volume-ratio of chloroform to water is 1:4, an error of about 3 per cent. is introduced. This ratio was used in all the experiments described. Test-tubes with glass stoppers were used, the test solution was first introduced, then chloroform, then 4 drops of dilute (1 : 1) hydrochloric acid, and finally a small drop of a concentrated solution of sodium nitrite to oxidise the iodine. The tubes were shaken for three minutes, allowed to stand for an hour in the dark, and then compared colorimetrically. Standard solutions were made up to contain 10, 20 and 40 mgrms. of iodine (as potassium iodide) per litre. The method is not suitable for concentrations higher than 40 mgrms. per litre, but concentrations as low as 0·125 mgrms. per litre can be used. The following salts in concentrations up to 200 grms. per litre had no effect on the results:—Sodium sulphate, magnesium sulphate and calcium sulphate. Sodium chloride (up to 15 grms.), calcium chloride (up to 12·5 grms.), and magnesium chloride (up to 10 grms. per litre) did not interfere. Larger amounts of these salts affected the results proportionally to the concentration, owing to their effect on the partition coefficient of the iodine. The following table shows the results obtained:

	Percentage loss of iodine in the presence of		
Concentration of salt Grms. per litre	Sodium chloride	Calcium chloride	Magnesium chloride
0·10	0·0	0·0	0·0
12·5	0·0	0·0	5
25	3·2	5	10·8
50	20	11·7	18·3
100	24·6	32·4	51·2
150	34·7	—	71·3
200	50	70·3	100
350	100	—	—

The results may be plotted graphically and a correction applied. Empirical formulae, calculated from the figures, give the corrected values as follows:—

$$\text{Sodium chloride}\ \frac{100a}{104{\cdot}05-0{\cdot}270b}=x$$

$$\text{Calcium chloride}\ \frac{100a}{104{\cdot}65-0{\cdot}373b}=x$$

$$\text{Magnesium chloride}\ \frac{100a}{105{\cdot}26-0{\cdot}526b}=x,$$

where x represents the corrected value, a the iodine-content as found in mgrm. per litre, and b the concentration of interfering salt in grms. per litre. Bromides, up to a concentration of 1·5 grms. per litre, have no effect on the results.

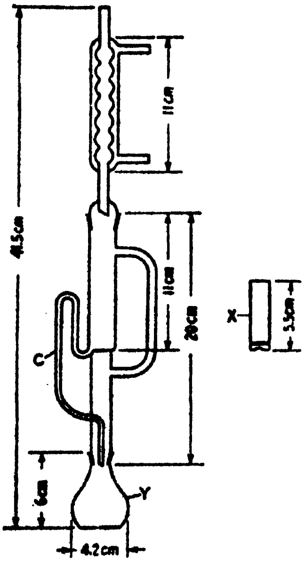
J. W. B.

Microchemical

Torsion Micro-balance. J. Donau. (*Mikrochem.*, 1933, 13, 155–164.)—The modification of the Nernst air-damped micro-balance previously described (ANALYST, 1931, 56, 342) has been further improved. The beam is made of duralumin instead of glass, and at the centre of gravity it is attached to a rider or carrier which is fixed to the quartz thread in two places, instead of being supported at only a single point. The beam is 7 cm. long, and at the ends there are two fixed riders which support the pans from quartz threads. These two riders or carriers, can be raised or lowered by a screw to adjust the sensitivity of the balance. The pointer, which is fixed in the middle of the beam, consists of a fine glass rod pulled out to a hair-fine tip where it reaches the scale; swings are read with a telescope. Apart from the disadvantage of small load-capacity (about 0·5 grm.), the advantages of the balance are the following:—Simplicity of construction, so that no cleaning or adjustment is necessary when it is set up correctly; the balance is much less sensitive to temperature effects than the Kuhlmann type, as the beam weighs only 1·5 grm. temperature equilibrium is reached almost instantaneously, weighing is much more rapid, and is complete in about 15 seconds. Ordinary riders are not used, but only small tares of known weight, so that the error of placing the rider at the wrong angle which can be quite appreciable in weighing with the Kuhlmann balance, does not occur. The weights should always be corrected for null point variation, which, however, is small.

J. W. B.

Micro-extractor. L. Titus and V. W. Meloche. (*Ind. Eng. Chem., Anal. Ed.*, 1933, 5, 286–288.)—The micro-extractor, which is of Pyrex glass, consists of the following parts: The lower part, S, was made from a 40-mm. tube with an ether-tight ground-glass joint, the inner member, R, of the joint being sealed to the condenser, and the outer member, A, sealed up to form a cup. The extraction thimble, T, was made from a 16-mm. tube, constricted as shown, with a shorter length of 15-mm. tube fitting by means of a ground joint into the end of the longer 16-mm. tube, and hooks were sealed at the top of the thimble to support it in the aluminium ring, E. Before use, the thimble is fitted with a filter-paper bottom; for this purpose, it is taken apart, an 18-mm. disc of No. 50 Whatman filter-paper, wetted with water, is placed over the lower end of the outer tube of the thimble, and forced into place by firmly pressing the shorter tube into the ground end of the larger tube. The weighing bottle, D, blown from soft glass, weighed 4 grms., and when in position in the apparatus, an annular clearance



of at least 1 mm. was found desirable between the mouth of the bottle and the thimble. During the functioning of the apparatus, it is necessary to keep the main joint slightly warm to prevent ether from condensing there; this was accomplished by passing one strand of No. 26 nichrome wire around the joint at P, and passing sufficient current to maintain it at 50° C.; a covering of adhesive tape (presumably "insulating tape" is meant) over the wire was found necessary to maintain satisfactory heating of the joint.

Method of use.—The bottle D and the sample (about 15 mgrms.) are weighed on a micro-balance with the usual precautions, and the sample is introduced into the thimble. Five ml. of pure ether are added to the bottle D, which is placed in the bottom part of the apparatus. The aluminium ring E is placed on the top edge of A, and the thimble is lowered into position. The cup A is then joined to the upper part of the extractor. The apparatus is evacuated to a pressure of about 20 cm. of mercury and the stopcock is closed. Current is passed through the heating wire, and such heat is applied to the cup A, by means of an electric heater-box, that the rate of condensation of ether is not high enough to cause the condensed ether to rise above the constriction in the thimble. After the extraction, the ether is removed from the apparatus under reduced pressure. After the gradual admission of air, the lower part of the extractor is detached, and the bottle D is removed and weighed, giving the weight of extract. Close agreement between the results of this and of the Soxhlet method was obtained in tests on samples of dry skim milk, casein and residues from the evaporation of lake water. A micro-extractor of the Soxhlet type is also described, but it gave less satisfactory results than the above. S. G. C.

Microchemical Tests IX. L. Rosenthaler. (*Mikrochem.*, 1933, **13**, 317–320.)—1. *Potassium perrhenate as a precipitant for alkaloids.*—The reagent precipitates benzene as well as veratrine (*C. Agte. Z. anong. Chem.*, 1931, **196**, 129) and a large number of other alkaloids. The alkaloids given below give a crystalline precipitate when a drop of a 1 per cent. solution is added to a drop of the aqueous solution of the alkaloid, or when a few crystals of the solid alkaloid are placed on the edge of the drop of reagent. *Aconite* gives small rods and needle-shaped crystals, some forming stars. *Alypine* forms branched needles and plates. *Berberine* forms stars and groups of small needles. *Brucine* forms small thick groups of needles. *Quinidine* at first gives an amorphous precipitate which slowly becomes crystalline, finally forming groups of small needles. *Diocaine* gives at first an amorphous precipitate, and then gives rosettes of leaf-shaped crystals. *Heroin* forms rosettes of many-cornered leaf-shaped crystals. *Hydrastinine* gives large irregular-shaped crystals. *Pantocaine* gives plates and groups of needles. *Strychnine* slowly forms prisms, some crossed, and forming stars. With the solid hydrochloride, prisms are also formed.

2. *Crystal precipitation with alkaline hydroxyquinoline.*—The reagent solution is a 10 per cent. solution of hydroxyquinoline in 30 per cent. acetic acid, treated with potassium hydroxide solution until the precipitate first formed dissolves. If the solution is not clear, it should be filtered through kieselguhr. A large number of metals are precipitated by the reagent. *Thallium* gives an amorphous

precipitate changing to the crystalline form. *Nickel* and *cadmium* give only an amorphous precipitate. *Chrome alum* (1 : 100) gives first an amorphous precipitate, and then groups of long fine needles which sometimes disappear again. *Copper sulphate* and *lead acetate* both react with the reagent to give crystals in dilutions between 1 : 10,000 and 1 : 20,000. *Calcium acetate* gives crystals in dilutions between 1 : 10,000 and 1 : 20,000, but barium and strontium are less sensitive; for barium acetate the limit of dilution lies between 1 : 500 and 1 : 750, and for strontium nitrate between 1 : 1000 and 1 : 2000.

3. *A sensitive test for thiocyanates.*—The test combines two known reactions—oxidation to hydrocyanic acid and the detection of this as silver cyanide (Melitzky and Koslowsky, *Mikrochem.*, 1929, **7**, 94). A drop of the solution under examination is mixed with a few drops of dilute sulphuric or acetic acid (acetic acid in the presence of chlorides), and a little potassium permanganate is added. The small glass container is covered with a cover glass holding a drop of the silver nitrate methylene blue solution of Melitzky on its under side. After a period of time, varying with the concentration, blue crystals of silver cyanide are formed. The limit of dilution is 1 : 100,000.

4. *Volatile amines and reagents for ammonia.*—All the tests for ammonia described by Feigl (ANALYST, 1933, **58**, 641), with the exception of the formation of a precipitate with Nessler's reagent, are also applicable to monomethylamine, dimethyl- and trimethyl-amine. Seven photomicrographs are given.

J. W. B.

Micro Gas Analysis and its Applications, especially in Biological Work (Collected References). H. Schwarz and F. Rappaport. (*Mikrochem.*, 1933, **13**, 235–274.)—The micro methods of gas analysis are described, with experimental details, and references are given to 14 text-books and pamphlets and to 27 original papers.

(i) *Methods involving measurement of gas volume.*—These include the Haldane method, its use for different gases and mixtures of gases, and its various modifications. The Krogh method for microscopic volumetric measurements, which is suitable for the measurement of the respiration of insects, is described. The useful but less accurate spirometric methods are mentioned. References are given for different types of nitrometers.

(ii) *Methods involving the measurement of gas pressure.*—These include the van Slyke, the Barcroft, and the Warburg methods, all of which are described in detail.

(iii) *Optical methods*, in which interference and refractive phenomena are measured, are briefly described.

(iv) *Thermo-electric methods.* (v) *Weighing and vapour tension* methods are described. (vi) Brief mention is made of other methods, and references are given to facilitate choice of apparatus.

J. W. B.

Detection and Determination of Small Amounts of Mercury (Collected References). F. Cucuel. (*Mikrochem.*, 1933, **13**, 321–364.)—The literature of the micro-chemistry of mercury is critically surveyed, and experimental details of many methods are given. There are five diagrams and 180 references.

I. The *qualitative* tests described are included under the following headings: (i) The amalgam test; (ii) aluminium test; (iii) the wire methods, in which the mercury is deposited on iron or copper wire, either by placing the wire in the test solution or electrolytically. The mercury may be finally identified by the iodine test. (iv) Crystal formation. Five tests are described for divalent, and 3 for monovalent mercury. (v) Spot tests, of which 7 are given. (vi) Tests on impregnated threads. (vii) Spectral analytical tests.

II. The *quantitative* methods include methods under the following headings:—(i) Volumetric methods; (ii) Colorimetric and nephelometric methods; (iii) Gravimetric methods, which include weighing the mercury as (*a*) sulphide, as (*b*) the complex $[HgI_4]$ $(Cu\mathit{en}_2)$ which is formed by precipitation with potassium iodide and copper ethylenediamine nitrate, and (*c*) deposition in metallic form on copper, platinum or gold; (iv) Spectrographic methods. (v) Micro-metric methods, in which the mercury is separated and distilled and its volume measured under the microscope; (vi) The methods of Bodnár, Szép and Stock (*J. Amer. Chem. Soc.*, 1926, **48**, 1815) are described in detail.

III. Details of methods are given for the detection and determination of mercury in urine and other organic and biological material.

IV. A section deals with the detection and determination of mercury in the atmosphere.

J. W. B.

Physical Methods, Apparatus, etc.

Gas-Holder for Constant Pressure. J. Lindner. (*Mikrochem.*, 1933, **13**, 313–316.)—A gas-holder of simple construction for maintaining constant pressure is described. It consists of two 10-litre aspirators; the upper aspirator is fitted up as a Marriotte flask, the glass water-outlet tube (which for convenience may be constructed in parts with rubber connections) passes down through a rubber stopper in the lower outlet hole of the lower aspirator, and is bent up, by means of a rubber connection, to reach the gas in the neck of the aspirator immediately under the gas-outlet tube. When the apparatus is filled, the gas escapes at a pressure depending on the difference in height of the bottom of the air-inlet tube of the upper aspirator (which is usually made to reach to the bottom of the upper aspirator) and the height of the end of the water-outlet tube from the higher to the lower aspirator, which is usually just below the gas outlet of the lower aspirator. The pressure may be adjusted by raising or lowering the upper aspirator. This aspirator is fitted with a short air-inlet, provided with a screw clip, and the water-outlet has an arm, also fitted with a screw clip, to reach only to the bottom of the lower aspirator, so that the gas-holder can be filled in the ordinary way by opening both these clips. The apparatus, set up in a suitable holder, is obtainable from P. Haack, Vienna.

J. W. B.

Precision Gas-Holder for Constant Pressure. H. O. Hohl. (*Mikrochem.*, 1933, **13**, 189–200.)—A patented gas-holder for constant pressure is described. It is constructed on the same principle as the apparatus described in the preceding abstract, but is made entirely of glass, so that any liquid may be used for the expulsion. It holds about 6 litres of gas. The apparatus is obtainable from P. Haack, Vienna.

J. W. B.

Reviews

RECENT ADVANCES IN PHYSICAL CHEMISTRY. By S. GLASSTONE, Ph.D., D.Sc. 2nd Edition. Pp. 498. London: J. & A. Churchill. 1933. Price 15s.

It is but two years since an appreciation of the merits of the first edition of this volume of Churchill's "Recent Advances" series was published in THE ANALYST (**1932**, **57**, 68), a fact which clearly demonstrates two things: one, the intrinsic merits of the work; and the other, the rapidity of the advances which are taking place in the realm of physical chemistry. Indeed, now that heavy hydrogen is being studied so much, a third edition will be needed almost before the ink is dry on the second. It is unnecessary to review the work again at length, and it suffices to point out the much new matter which has been included and some which has been excised to make room for it. The chapter on solubility has gone; perhaps one may linger in regret because it was so interesting and useful. In its place is a discussion of wave mechanics, calculation of energy of activation, nuclear disintegration, surface potentials, surface mobility, the kinetics of photochemical reactions, adsorption both activated and continuous, the rotation of dipole moments and the study of molecular beams.

We think it was Kant who said that the amount of true science in any matter was strictly proportional to the amount of mathematics in it. It this be so, there is much truth in *Recent Advances in Physical Chemistry*, and much more truth in the second edition than in the first. We must congratulate Dr. Glasstone on the readableness of his work, despite the complexities of its subject-matter. He greatly helps those of us who do not specialise in this field to follow the almost bewilderingly rapid strides of those who do: would that he helped us more easily to remember the mathematical details! H. E. COX

INTRODUCTION TO PHYSICAL CHEMISTRY. By ALEXANDER FINDLAY. Pp. vii+492. London: Longmans, Green & Co. Price 7s. 6d.

On the cover of this book it is stated that its aim "is to provide a text-book which shall not only serve as an introduction to the study of physical chemistry, but shall also carry the student on to such a point that he can read with profit the numerous special monographs now available. The work is designed more especially to meet the needs of the student of chemistry who desires to build his later specialised study on a broad foundation." This it is likely to do, which is more than can be said of many books which are obviously designed to enable students to pass certain examinations and then to pay the minimum of attention to a boring subject.

Professor Findlay has the gift of making a difficult subject interesting. By adopting a somewhat historical treatment and giving the full names of the many workers who have helped to unravel the mysteries of the relations of electrons, protons, neutrons, atoms, and molecules to one another in time and space, he has succeeded in humanising physical chemistry.

Many of us must either remember hearing the Faraday Lecture of Wilhelm Ostwald, in which he sought to explain all that we then knew of chemistry without invoking the aid of atoms, or have read his Chemical Conversations, with their

Berkeleyan repudiation of substance. The researches of many workers in different tracts of the borderland between physics and chemistry have not only fully established the atoms, but have demonstrated their complexity. How this was done, and the light which such work as that of Jean Perrin on the curious movement of small particles in a liquid, discovered by Robert Brown in 1827, threw on facts hidden in the lumber room of science, is well described in the earlier chapters of this book. It may here be noted that Waterson's earliest development of the kinetic theory of gases in 1845, which was dug out of the archives of the Royal Society and made public by Lord Rayleigh in 1892, is mentioned.

Towards the end of last century inorganic chemistry seemed a dead subject, and physical chemistry merely a barren field yielding only a few weeds uninteresting to right-minded chemists or physicists. The brilliant light thrown on the constitution and spacial configuration of organic compounds, by researches in which chemistry was aided by the polarimeter and goniometer, had diverted most chemists from the basic facts of the subject, except as applied to a large and tractable group of compounds of a very few elements. The periodic law of Newlands, Mendeléef and Lothar Meyer was found to present almost as many anomalies as coincidences, and the similarities and differences of the known elements were inexplicable. The discovery of the rare gases and of radioactive elements, with J. J. Thomson's work on the electrical conductivity of gases, opened up a new field of speculation for those blessed with imagination. The application of the gas laws to solutions and the development of Faraday's conception of ions broke down for ever the barriers between physics and chemistry, greatly to the advantage of both sciences. All these things, and the energetic conditions and time relationships governing chemical reactions, with the effect of chemical constitution on physical behaviour of chemical entities, are ably set forth by Professor Findlay.

The present grave danger is that students whose temperament should lead them to take mathematics as their principal subject may be tempted to build on chemical observations, made uncritically, a vast and unstable superstructure of formulae, forgetting that the chemist's place is the laboratory, not the armchair, and that pens and paper are not his principal pieces of apparatus. The great physical chemists have all been good experimenters.

On reading on p. 65 the statement "it has been found that when water vapour has been very carefully freed from dust particles its temperature may be lowered considerably below the point of condensation before liquefaction takes place," one supposes that the author's reading on hygroscopic nuclei has been confined to the work of his countryman, Aitken, and has not included that of Wigand, Nolan and other later workers, who have shown that dust particles do not act as condensation nuclei.

An omission which is all the more remarkable, in view of the wide range of subjects treated and of the very up-to-date character of the book, is the absence of all reference to the highly interesting and important metallic state, concerning which sufficient is known for the author, had he been so minded, to have given us a few illuminating paragraphs.

It is hardly correct to describe chloroform, as the author does on p. 148, as being insoluble in water, when *aqua chloroformi* is a well-known pharmaceutical preparation; the experiment there described does not seem to show the desired result until after some days.

The book appears to be remarkably free from errors and misprints; it can be confidently recommended to the student who really wants to know, and to those of us whose work lies mostly in other branches of chemistry, but who wish to have a readable manual from which to obtain information of a reliable kind on points of physical chemistry which may bear on our own problems, with references enabling us to read what the original authors themselves had to say about their work.

The publishers are to be congratulated on the production of this important work in an attractive form and at a very low price. J. H. COSTE

THE PHYSIOLOGICAL EFFECTS OF RADIANT ENERGY. H. LAURENS, Ph.D. American Chemical Society Monograph. Pp. 610. New York: The Chemical Catalog Company, Inc. 1933. $6.00.

This is a monumental review of published work on the effects on the human body, and on some other organisms, of ultra-violet, visible, and infra-red radiation. The principal criticism of this book is anticipated by the author himself in his preface, where he says: "No doubt many readers will be annoyed at the inconclusiveness of some of the statements and arguments." Some sections do indeed present long bewildering accounts of numerous experiments carried out by different workers under different experimental conditions, often imperfectly controlled and only qualitatively recorded, leading to inconsistent, if not quite contradictory, conclusions. But this, of course, is hardly the author's fault, except that his passion for completeness has led him to include work which, on internal evidence, might have been rejected as comparatively worthless. Some attempt might also have been made to summarise the evidence at the end of each chapter. At least, the method followed has the merit of demonstrating most convincingly the need for much more accurate and carefully controlled work in the field, and it is to be hoped that in later editions it will be possible to present a less confusing picture of the state of our knowledge.

In so far as the author presents his own views at all, they are extremely sane. He points out that the undoubtedly specific effect of ultra-violet radiation in the treatment of rickets, and other established cases of the benefits accruing from light therapy, have led to indiscriminate and inadequately controlled use of solar and artificial radiation for all manner of complaints. The sun is "an heroic remedy," whilst artificial sources, and particularly quartz mercury-vapour lamps, are by no means perfect substitutes for sunlight. It would appear that in many cases the value of irradiation lies chiefly in the penetrative power of the short infra-red and visible rays, producing a rise of temperature several mm. below the skin. Carbon arcs may replace the sun for this purpose, but the light from mercury-vapour lamps is relatively deficient in infra-red, and contains ultra-violet radiations, extending far beyond the limits of the solar spectrum, and not by any means necessarily beneficial.

After a brief introduction, the book begins with a long chapter on the physics of radiant energy, dealing with the measurement of radiation and the characteristics of sources, natural and artificial. There follow chapters on the effects on the skin, on wounds and certain skin diseases, on the eye, on the circulatory system and the blood, on metabolism (five chapters), and on body temperature and respiration; the next chapter deals with photodynamic sensitisation, others with the effects on tuberculosis, and on bacteria, toxins, and so on; to conclude there is a short and halting chapter on the mode of action of radiant energy on physiological and pathological processes. This arrangement seems susceptible of improvement, since it leads to some scattering of information on a particular subject: for example, tuberculosis is the subject of Chapter XI, but skin tuberculosis is relegated to Chapter IV; skin and subcutaneous temperatures are mentioned in six different chapters.

It is a curious fact that the word "colour" does not even appear in the index; there is no mention of observations on the effect of colours, for example, of wall-coverings, on well-being; but, perhaps, this is relegated to a later volume on the psychological effect of radiant energy?

On the whole, however, the book is well conceived and accurate, though a few sections bear evidence of careless proof-reading. The historical survey of the chemistry of vitamin *D*, for example—a subject outside the main field of the work—is excellently presented, but within ten pages occur such errors as "ergot" for "ergosterol" (p. 411), omission of the word "destroyed" (p. 416), "solute" for "solution" (p. 421). It is a little confusing, moreover, when hypotheses later abandoned by their authors, or disproved, are presented as though they were still accepted.

There is a bibliography of nearly a thousand references, including many of recent date, a good author index, and fairly complete subject index.

E. LESTER SMITH

PRACTICAL PHYSIOLOGICAL CHEMISTRY. Ninth Edition. S. W. COLE, M.A. Pp. xii+419. Cambridge: W. Heffer & Sons, Ltd. 1933. Price 12s. 6d.

Reviewing a previous (seventh) edition of this book some years back (ANALYST, 1926, **51**, 273), I commented that a new edition of "Cole" must always mark a minor epoch for chemists whose work brings them at any point in touch with physiological problems. That remark is even truer of the ninth than it was of the seventh edition, for the eighth edition of 1928 has here not only been fully revised, but almost wholly re-written. This has had several very valuable results, not least of which is a reduction in the number of pages from nearly 500 to a little over 400, a result that has been achieved by technical devices of the publisher and printer, as well as by the author's revision.

It may be noted with satisfaction that the "literals" that disfigured the seventh edition to a rather unnecessary extent appear to be absent from the new one, as far as a cursory examination reveals; also that some of the minor errors found in the seventh edition, and cited in the previous review, have been either corrected or avoided altogether in the course of the revision.

The author, however, still persists in attributing to cholesterol a melting point three degrees lower than that of pure specimens, and evidently differs from the reviewer as to the advisability of introducing students to the Donnan membrane equilibrium theory. Nevertheless, in my opinion, it is of such importance in biochemistry that its introduction to students at the earliest possible moment ought to be attempted. The same remarks apply to the concept of oxidation-reduction potentials, which has become of increasing prominence during the last few years; this might well have been discussed, however briefly, in Chapter XI which is concerned with "Oxidising and Reducing Mechanisms." The appropriateness of such discussion must have been in Dr. Cole's mind, for this chapter contains the sole reference to the concept in question. He writes that the energy conditions of oxidation and reduction re-actions are related to the relative affinities for hydrogen of the oxidised and unoxidised re-actants, and that "this is related to what is known as 'oxidation reduction potential' which cannot be discussed here."

This text-book has for many years been one of the most useful for students of biochemistry, and its revision has certainly in no way diminished its utility. Moreover, like all good text-books, it contains information and suggestions of value to the qualified practitioner as well.

A. L. BACHARACH

Publications Received

BRITISH STANDARDS INSTITUTION

BRITISH STANDARD SPECIFICATIONS (1933).

No. 515. CRUDE CARBOLIC ACIDS.
No. 516. DISTILLED CARBOLIC ACIDS.
No. 517. CRESYLIC ACID OF HIGH ORTHOCRESOL CONTENT.
No. 521. CRESYLIC ACID (50/55 PER CENT. METACRESOL).
No. 522. ORTHOCRESOL, METACRESOL AND PARACRESOL.
No. 523. PHENOL.
No. 524. REFINED CRESYLIC ACIDS (GRADES A AND B).
No. 526. BRITISH STANDARD DEFINITIONS OF GROSS AND NET CALORIFIC VALUE.

Price 2s. each. Post free 2s. 2d., except No. 526 which is 1s., post free 1s. 2d. To be obtained from the Publications Department, 28, Victoria Street, London, S.W.1.

THE CONTROL OF WATER SOFTENING AND BOILER WATER CONDITIONING. Issued by Imperial Chemical Industries Ltd., London, S.W.1. Pp. 39.

CONTENTS.—Introduction—Summary of Tests—Control Tests for Water Softening—Alternative Estimation of Hardness of Water—Boiler Feed Water Conditioning—Analyses for Blowdown Control—Table of Daily and Weekly Tests—Bibliography.

THE COLORIMETRIC DETERMINATION OF OXIDATION–REDUCTION BALANCE. The British Drug Houses, Ltd., Graham Street, London, N.1. (A copy will be supplied by the British Drug Houses, Ltd., to any chemist who cares to write to them for one.)

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THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

A JOINT Meeting of the Society of Public Analysts and Other Analytical Chemists with the Food Group of the Society of Chemical Industry was held on Wednesday, February 7th, at the Chemical Society's Rooms, Burlington House. The President of the Society of Public Analysts, Mr. F. W. F. Arnaud, was in the chair.

Certificates were read in favour of: Donald Burton, M.B.E., D.Sc., F.I.C., Arthur Sereld Houghton, M.Sc., F.I.C., Homi Ruttonji Nanji, B.Sc., Ph.D., D.I.C., A.I.C., Harold Overton, B.Sc., John Milner Russell, B.Sc., and Walter Frederick Waters, B.Sc., A.I.C.

The following were elected members of the Society of Public Analysts:—Sydney Emsley, B.Sc., F.I.C., George Frederick Hall, M.B.E., B.Sc., A.I.C., Walter Maurice Keightley, A.I.C., Dorothy Mary Mathews, B.Sc., Reginald Percival Page, F.I.C., Hilda Mary Perry, M.Sc., A.I.C., Arthur Dudley Powell, A.I.C., Winifred Ethel Smith, B.Sc., A.I.C.

The following papers were read and discussed :—"The Analysis of Fruit and Fruit Products," by E. B. Hughes, M.Sc., F.I.C., and Miss A. E. Maunsell, B.Sc.; "The Examination of Fruits and Jams by Lead Precipitation," by C. L. Hinton, F.I.C.; and "Equalisation of Temperature in Electric Ovens," by F. G. H. Tate, F.I.C.

NORTH OF ENGLAND SECTION

THE Ninth Annual General Meeting of the Section was held in Manchester on February 10th, 1934. The attendance was thirty-nine; the Chairman (Mr. J. Evans) presided.

The Secretary read the report and financial statement for 1933, which were adopted.

The following appointments for the ensuing session were made:—*Chairman:* Prof. W. H. Roberts; *Vice-Chairman:* A. R. Tankard; *Committee:* W. G. Carey, G. D. Elsdon, H. B. Marston, H. M. Mason, A. Scholes, J. G. Sherratt, C. J. H. Stock; *Honorary Auditors:* U. A. Coates, J. W. H. Johnson; *Honorary Secretary and Treasurer:* J. R. Stubbs.

An address was given by Prof. T. P. Hilditch, D.Sc., F.I.C., on "Some New Applications of the Elaidin Reaction in the Examination of Fatty Oils."

Dr. Dunn conveyed the congratulations of the Section to Mr. J. Evans on his nomination to the office of President of the Society.

A resolution was passed expressing deep regret at the death of Mr. William Marshall, who was an Auditor of the Section from its inauguration, and conveying sympathy to his relatives in the loss they have sustained.

The Examination of One Thousand Milks by the Hortvet Freezing-Point Process

BY J. R. STUBBS, M.SC., F.I.C., AND G. D. ELSDON, B.SC., F.I.C.

(Read at the Meeting of the North of England Section, October 14, 1933)

MANY papers have appeared from time to time giving the results of the examination of milk by the freezing-point test. In some instances the workers have examined a considerable number of samples; for example, Stoecklin tested 2500, Gronover and Türk 650, Reicher 467, Andrew 270, MacLaurin 270, Bailey and his collaborators 240, and others have examined a smaller number of samples.

Some of these milks were obtained from individual cows, and others from herds. In most cases, however, the details of the work and arrangements of the results have not been given in a form which is easily available for information; the figures have not usually been recorded in complete tables, and frequently only the extremes and means have been stated. Furthermore, the work that has been done has related mainly to milk derived from Continental, American or Australian cattle.

So far as we are aware, only one systematic investigation has been published in Great Britain, that by Tocher (*Variations in the Composition of Milk,* 1925; ANALYST, 1926, **51**, 146). Tocher examined the milk of 676 individual cows from various districts of Scotland. The results of this work are of limited value, because many of the milks, at the time of examination, were not quite fresh; it does not appear that the acidities of all the samples were ascertained, and therefore it is impossible to distinguish those that were fresh from those in which sourness had set in.

The present communication deals with the examination, by the freezing-point test, of 1000 milks, a few of which were obtained from individual cows, but the great majority from herds. Most of the samples were taken under the Food and Drugs (Adulteration) Act, in the County of Lancaster, and the others (330 in number) were taken as "appeal-to-cow" samples from farms situated in the County of Lancaster or in neighbouring counties. The 670 samples taken in the ordinary way under the Food and Drugs Act were considered to be genuine from the results of examination, but no sample has been excluded from the figures here given unless an "appeal-to-cow" sample has given a figure materially greater than the one excluded. It is, therefore, possible that one or two samples have been included which contain traces of extraneous water, but no sample has been excluded from these records unless it was definitely known to be adulterated.

In accounts of the work of various observers who have investigated the freezing-point of milk there appears to be a very serious lack of precise information as to the apparatus used, the method of procedure and the corrections applied. The freezing-points recorded in this paper were determined by the Hortvet apparatus, following the instructions laid down in the A.O.A.C. *Methods of Analysis*, third edition, 1930, p. 219, and with no corrections other than those therein mentioned. The freezing-points and averages are given to the nearest third decimal place. The acidity of all samples was determined, and was sufficiently low to be without material effect on the freezing-point.

The results for the "appeal-to-cow" samples are included in the total of 1000 samples, but they are also given separately. The fact that the two sets of results—those relating to "appeal-to-cow" samples only, and those concerning the whole of the 1000 samples—are very similar lends support to the opinion that the whole of the samples were genuine.

TABLE I.

FREEZING-POINT DEPRESSIONS: ALL SAMPLES

	"Appeal-to-cow" samples	Other samples	All samples
No. of samples	330	670	1000
Average	0·545	0·544	0·544
Extremes	0·529 0·563	0·530 0·563	0·529 0·563

Two samples, taken after supervised milking, have been met with which have had a freezing-point depression as small as 0·529° C. Both samples were taken in 1930—one in October and the other in November. This was near the beginning of the period over which the present investigation extends, and very few figures had, at that time, been collected. If these small depressions had occurred at a later date, the supervised milkings would have been repeated under stricter control. This has since been done in similar cases, with the result that a greater depression than 0·529° C. has invariably been obtained.

MORNING AND EVENING MILKS.—In most cases it was known whether the samples were from the morning or evening milking. The results have been tabulated in Table II, showing the figures for morning and evening milks separately. Consideration of Table II seems to show that there is no significant difference in any case.

TABLE II

FREEZING-POINT DEPRESSIONS: MORNING AND EVENING MILKS

	Morning samples	Evening samples	Unknown	Total
No. of samples ..	440	500	60	1000
Average	0·545	0·544	0·544	0·544
Extremes ..	0·530 0·563	0·529 0·563	0·530 0·556	0·529 0·563

FREQUENCIES.—It is now generally admitted that, for statistical purposes, extremes and means have only a limited value. It is more valuable to know, in addition, how frequently a certain figure has been found, and the results for the whole of the milks examined by us have, therefore, been arranged to show the frequencies. These are classified in Table III. Table IV shows the frequencies of the milks for morning and evening samples separately.

TABLE III

FREEZING-POINT DEPRESSIONS: FREQUENCIES—ALL SAMPLES

Freezing-point depressions		"Appeal-to-cow" samples	Other samples	All samples
0·529	0·530	4	2	6
31	2	1	3	4
3	4	5	15	20
5	6	12	24	36
7	8	23	45	68
9	0·540	33	88	121
0·541	2	37	88	125
3	4	56	101	157
5	6	33	106	139
7	8	38	71	109
9	0·550	35	48	83
0·551	2	11	40	51
3	4	17	17	34
5	6	10	13	23
7	8	5	3	8
9	0·560	5	5	10
0·561	3	5	1	6
		330	670	1000

TABLE IV

FREEZING-POINT DEPRESSIONS: FREQUENCIES—MORNING AND EVENING MILKS

Freezing-point depressions		Morning samples	Evening samples	Unknown samples	Total samples
0·529	0·530	2	3	1	6
31	2	2	2	—	4
3	4	10	9	1	20
5	6	14	21	1	36
7	8	31	36	1	68
9	0·540	43	67	11	121
0·541	2	53	61	11	125
3	4	62	83	12	157
5	6	68	65	6	139
7	8	48	55	6	109
9	0·550	39	39	5	83
0·551	2	23	26	2	51
3	4	11	21	2	34
5	6	13	9	1	23
7	8	7	1	—	8
9	0·560	9	1	—	10
0·561	3	5	1	—	6
		440	500	60	1000

SOLIDS-NOT-FAT.—The great value of the freezing-point test for milk, as compared with other tests, is that the figure obtained appears to be quite independent of that for the solids-not-fat. Almost all investigators who have considered the matter concur in this view. In other words, it would appear that a normal milk is not one having solids-not-fat of, say, 8·5 to 9·0 per cent., but one having a freezing-point depression of about 0·54° C.

In Table V the figures for freezing-point depressions and solids-not-fat of all the samples have been set out; Table VI gives the corresponding figures for the 330 "appeal-to-cow" samples, and Table VII those for the 670 milks, other than "appeal-to-cow" samples, considered to be genuine. It will be seen that there is no obvious relationship between the solids-not-fat and the freezing-point depression, and that this applies, in the case of the freezing-point, both to the extremes and means of the figures observed.

TABLE V

FREEZING-POINT DEPRESSIONS AND SOLIDS-NOT-FAT; ALL SAMPLES

Solids-not fat Per Cent.	No. of samples	Freezing-point depressions		
		Average	Least	Greatest
7·6–7·9	4*	0·545	0·535	0·555
8·0	6	0·544	0·537	0·552
8·1	5	0·546	0·529	0·559
8·2	22	0·543	0·536	0·550
8·3	36	0·543	0·533	0·552
8·4	62	0·543	0·529	0·559
8·5	95	0·544	0·531	0·563
8·6	103	0·543	0·530	0·557
8·7	128	0·544	0·533	0·563
8·8	156	0·543	0·530	0·561
8·9	147	0·545	0·533	0·561
9·0	116	0·547	0·533	0·563
9·1	61	0·546	0·532	0·559
9·2	37	0·545	0·531	0·556
9·3	9	0·548	0·545	0·556
9·4	8	0·546	0·538	0·560
9·5 and 9·6	5†	0·547	0·539	0·550
	1000	0·544	0·529	0·563

* 1 each of 7·6, 7·7, 7·8 and 7·9 per cent. † 3 of 9·5 per cent., 2 of 9·6 per cent.

This absence of correlation between freezing-point depressions and solids-not-fat is what would be expected, since, as appears to be the case, the freezing-point depends on the osmotic pressure of the blood of the cow and not on the total amount of solids in solution in the milk; a deficiency in one ingredient of the solids-not-fat, usually lactose, is balanced as regards osmotic pressure by an increase in another constituent, *e.g.* mineral salts, and a small amount of the latter has the same effect in depressing the freezing-point as a much larger amount of lactose. Hence the solids-not-fat may be low owing to a deficiency in lactose, and the effect on the freezing-point, but not on the solids-not-fat, may be counterbalanced by a small amount of mineral salts.

TABLE VI

FREEZING-POINT DEPRESSIONS AND SOLIDS-NOT-FAT; "APPEAL-TO-COW" SAMPLES

Solids-not-fat Per Cent.	No. of Samples	Freezing-point depressions		
		Average	Least	Greatest
7·6–7·9	3*	0·543	0·535	0·555
8·0	5	0·542	0·537	0·550
8·1	2	0·546	0·529	0·538
8·2	7	0·546	0·541	0·550
8·3	12	0·542	0·533	0·551
8·4	21	0·542	0·529	0·551
8·5	31	0·544	0·534	0·553
8·6	36	0·543	0·534	0·557
8·7	46	0·545	0·536	0·563
8·8	56	0·545	0·530	0·561
8·9	40	0·547	0·534	0·561
9·0	38	0·547	0·533	0·563
9·1	18	0·547	0·538	0·559
9·2	9	0·544	0·531	0·555
9·3–9·5	6†	0·551	0·545	0·560
	330	0·545	0·529	0·563

* 1 each of 7·6, 7·7 and 7·9 per cent. † 1 of 9·3 per cent., 4 of 9·4 per cent., and 1 of 9·5 per cent.

TABLE VII

FREEZING-POINT DEPRESSIONS AND SOLIDS-NOT-FAT; SAMPLES OTHER THAN "APPEAL-TO-COW" SAMPLES

Solids-not-fat Per Cent.	No. of samples	Freezing-point depressions		
		Average	Least	Greatest
7·6–8·0	2*	0·552	0·552	0·552
8·1	3	0·554	0·547	0·559
8·2	15	0·542	0·536	0·546
8·3	24	0·544	0·536	0·551
8·4	41	0·544	0·533	0·559
8·5	64	0·543	0·531	0·563
8·6	67	0·542	0·530	0·553
8·7	82	0·544	0·533	0·557
8·8	100	0·542	0·530	0·555
8·9	107	0·544	0·533	0·559
9·0	78	0·546	0·535	0·554
9·1	43	0·546	0·532	0·559
9·2	28	0·545	0·535	0·556
9·3	8	0·547	0·542	0·550
9·4	4	0·543	0·538	0·548
9·5 and 9·6	4†	0·547	0·539	0·550
	670	0·544	0·530	0·563

* 1 each of 7·8 and 8·0 per cent. † 2 each of 9·5 and 9·6 per cent.

MONTHLY VARIATIONS.—Stoecklin (*Ann. Falsif.*, 1911, 4, 232), from his examination of 2500 samples of milk, was of the opinion that the freezing-point depressions varied little from 0·550 either in winter or in summer. Buchanan and Lowman (*World's Dairy Congress*, 1928, p. 725) suggest that change in food, such as that from the autumn to the less nutritive spring growth, causes an osmotic disturbance, and so affects the freezing-point depression. But their conclusions appear to be based on a comparatively small number of samples. Beyond these, very little appears in the literature dealing with seasonal variations in the freezing-point depression of milk.

The figures obtained during the present investigation have been arranged according to the months in which they were produced. The period covered is from December, 1929, to September, 1933. The results are set out in Table VIII, from which it will be seen that the variations between the different months are insignificant, and such differences as occur do not seem to follow any obvious rule.

TABLE VIII

FREEZING-POINT DEPRESSIONS: MONTHLY VARIATIONS

Month	No. of samples	Freezing-point depressions		
		Average	Least	Greatest
January	51	0·543	0·530	0·559
February ..	123	0·543	0·530	0·561
March	78	0·544	0·531	0·559
April	70	0·546	0·533	0·563
May	82	0·544	0·535	0·563
June	69	0·546	0·535	0·560
July	116	0·545	0·535	0·559
August	77	0·545	0·533	0·556
September ..	62	0·544	0·534	0·557
October	114	0·545	0·529	0·561
November ..	91	0·544	0·529	0·555
December ..	67	0·544	0·530	0·559
	1000	0·544	0·529	0·563

TABLE IX

FREEZING-POINT DEPRESSIONS: JUNE TO SEPTEMBER, 1933

Month	No. of samples	Freezing-point depressions		
		Average	Least	Greatest
June, 1933 ..	35	0·545	0·535	0·560
July ,, ..	71	0·546	0·535	0·559
August ,, ..	53	0·545	0·533	0·555
September ,, ..	29	0·544	0·530	0·557
	188	0·545	0·530	0·560

The weather during the months of June, July, August, and September of 1933 was exceptionally dry and hot, and there was an unusually large amount of bright sunshine. It was, therefore, thought that it would be useful to extract the figures for freezing-point depressions obtained during these months (Table IX) and to compare them with those relating to the corresponding months recorded in Table VIII. It will be seen that the abnormal weather did not materially affect the freezing-point depressions.

SUMMARY.—As a result of the examination of one thousand milks by the Hortvet cryoscope an average freezing-point depression of 0·544° C. has been found, with extremes of 0·529° C. and 0·563° C. No material difference has been found between morning and evening milks or between milks produced in different months of the year, and no apparent correlation has been found between the freezing-point depression and the amount of solids-not-fat present.

Previous figures have been obtained with the Hortvet apparatus by Hortvet and Bailey, who found for the average, 0·545° C., with extremes of 0·530° C. and 0·566° C.

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The Excretion of Aloes

BY G. F. HALL, M.B.E., B.SC., A.I.C., AND W. M. KEIGHTLEY, A.I.C.

(*Read at the Meeting, December* 2, 1933)

IN our paper on the detection and estimation of aloes in *post-mortem* tissues (ANALYST, 1933, 58, 518), we have related a case resulting in death, the cause of which was an overdose of aloes, though the symptoms suggested some powerful toxic drug.

In the event of further cases of this type, where death has not occurred, or does not ensue, recourse must be had to examination of excreta. Since the faeces, containing most, if not all, of the unabsorbed aloes, would necessarily have been lost, we considered the desirability of examining the urine with a view to determining whether any absorbed aloes was excreted in that fluid, and whether it could be found there after a reasonable lapse of time. The condition of the drug and the probable manner of absorption were also investigated.

THE METHOD OF DETECTION AND ESTIMATION.—Slight modifications of our original method (*loc. cit.*) were rendered necessary when using large volumes of liquid. The urine was slightly acidified with acetic acid and then evaporated to a small volume in a porcelain basin over a low flame. Quantities of 200 ml. were usually taken and evaporated to 15 ml. or thereabouts, according to the solids-content, the evaporation being taken as far as possible without charring. To the residue was added sufficient alcohol to give a concentration of 60 per cent. in the mixture; the whole was then stirred, and the stirring was repeated after the addition of excess of a slightly acid, saturated solution of lead acetate in 60 per cent. alcohol, this solution being added warm to increase its concentration and thus prevent unnecessary dilution. After standing for a few minutes the mixture was filtered through a Buchner funnel containing a layer of asbestos fibre and, after the minimum amount of washing, hydrogen sulphide was passed through the combined filtrates until the excess of lead was precipitated, and then for some minutes longer, such treatment still further reducing the colour of the solution. The lead sulphide was removed by filtration, and aliquot parts of the clear liquid were taken for the detection and estimation of aloes by the modified Schoutelen and Bornträger tests previously described. In this case, however, it is advantageous in the Bornträger test to boil the liquid with a few drops of hydrogen peroxide after boiling with ammonia.

The following tables give a summary of results obtained in the examination of the urine of three persons, after taking Curaçao aloes.

It may be remarked here that in experiments recorded in Table III large quantities of liquid were consumed during the period of testing.

TABLE I

BLANK TEST

Aloes added Mgrms.	Volume ml.	Aloes found Total Mgrms.	Aloes found Unhydrolysed Mgrms.
0	200	0	0
10	200	10	8

TABLE II

Subject: Normal. Diet: Solid, normal. Liquid reduced. Aloes taken: 200 mgrms.

Urine Time after taking of drug Hours	Urine Volume ml.	Aloes found Total Mgrms.	Aloes found Unhydrolysed Mgrms.
8	220	5	1
13	220	0·5	0·4
19	220	<0·5	0·2
100	200	No reaction	No reaction

TABLE III

Subject: Normal. Diet: Solid, vegetarian. Liquid increased.
Aloes taken: 200 mgrms.

Urine Time after taking of drug Hours	Urine Volume ml.	Aloes found Total Mgrms.	Aloes found Unhydrolysed Mgrms.
8	340	—	1·0
9½	120	—	1·2
10½	620	—	1·2
13½	490	—	+
19	320	—	?
22	210	—	No reaction
25	230	—	Not examined
31½	380	—	+

TABLE IV

Subject: Constipated. Diet: Solid, normal. Liquid normal.
Aloes taken: 200 mgrms.

Urine		Aloes found	
Time after taking of drug Hours	Volume ml.	Total Mgrms.	Unhydrolysed Mgrms.
5	—	—	—
9	120	2·5	0·2
13	200	11	1·0
16	90	+	+
18	200	+	+
36	200	—	0·5
60	200	—	0·7

These Tables show that aloes is definitely excreted in the urine in both unhydrolysed and hydrolysed forms. It will be seen from the blank test that aloes, during treatment of the urine, undergoes negligible hydrolysis. The last column suggests that excretion of unhydrolysed aloes may possibly be more or less regular and persistent during three days after an intake of not more than the maximum therapeutic dose.

Generally speaking, the greatest excretion (chiefly hydrolysed) takes place about 10 hours after administration of the drug. This time is essentially modified by the period of retention of the bulk of aloes, which depends upon the condition of the individual.

GENERAL CONCLUSIONS.—A considerable portion of the drug excreted has been hydrolysed, and it may be assumed that this does not take place in the stomach (aloes being relatively stable in dilute acids), but that progressive hydrolysis occurs during passage through the intestines; first, in the small intestine, as the result of alkaline action; and then, in the larger intestine, owing more probably to bacterial or enzymic action. Since gastric hydrolysis is negligible, the amount of food in the stomach at the time of ingestion does not influence the state of the aloes found excreted; yet from a full stomach there may be a greater amount of absorption. Whatever the quantity absorbed here, it is probably excreted unhydrolysed in the urine.

As the hydrolysis occurring in the small intestine is either slight or incomplete, absorption, if occurring here, is of partly hydrolysed material. Probably the greatest absorption occurs in the large intestine, and, in the main, this is fully hydrolysed drug. Later, this is excreted relatively rapidly through the kidneys. It seems probable, in the event of excessive doses of the drug being taken, that the amount of absorption would be sufficient to allow of the detection of the aloes when the physician is consulted.

It has been shown previously (*loc. cit.*) that aloes excreted in the faeces is almost completely hydrolysed, and, furthermore, that the bulk of the administered dose is thus excreted in a comparatively short time. On the other hand, after the peak in urine excretion has been passed, small amounts, consisting mainly of unchanged glucoside, are still present; and, since the modified Schoutelen reaction (for unhydrolysed drug) is more delicate and distinctive than the Bornträger reaction (for hydrolysed drug), tests on the urine offer many advantages, particularly after the early period of intense drug excretion has passed.

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DISCUSSION

The PRESIDENT said that this was not only a very interesting paper but was also useful, because occasions did arise when it was important to have methods that would enable a view to be formed of the probable dose of aloes taken some hours previously.

Mr. C. E. SAGE said that there were two aspects of the subject which made him appreciate the work done by the authors of the paper, namely, the analytical one, in which a pill or pills were sent for analysis and the ingredients needed identification, and the toxicological one in which aloes would have to be identified after mixture with other substances. In the former the identification was generally easy and definite, but in the latter contingency the aloes might be mixed with other drugs containing emodin or anthraquinone constituents. He hoped the authors' work had made it possible to distinguish between aloes and, say, cascara, senna, and rhubarb, but if it were possible to discover the presence of hydrolysed aloin three days after the administration of the drug, they had arrived at something really valuable.

Had the authors any evidence to show whether the application of chrysarobin ointment to the skin had a similar effect, and had they any way of differentiating the aloes employed, for there were great variations in the composition of that drug?

Dr. G. ROCHE LYNCH said that there was no doubt that any method by which one could get some idea of the amount of aloes taken from the amount excreted was of great value. He had only one question to ask the authors: Why had they used the lead acetate in the alcohol stage? In toxicological work he had frequently added the lead acetate to the original urine in aqueous solution. There might be some valid reason that the authors had mentioned and that he had not followed, but he thought that they would get a better clearance of the urine.

Mr. KEIGHTLEY said that the filtration of aqueous acid or alkaline solutions containing lead acetate was attended by loss of aloes due to adsorption on precipitated proteins. Such conditions did not obtain in the presence of alcohol. It had been found necessary to have aloes in slightly acid alcoholic solution prior to the addition of any protein precipitant.

Mr. HALL, replying to Mr. Sage's query as to the distinction between aloes, cascara, senna, and rhubarb, said that senna and rhubarb did not give the brilliant golden "aloes fluorescence." Hubbard (ANALYST, 1917, **42**, 277) had stated that the borax test was capable of distinguishing aloes from other emodin-containing drugs, though cascara might give a similar, though not identical, fluorescence. They had found that the cascara fluorescence was not nearly so intense as the aloes fluorescence; a reaction was given by a sample of Curaçao aloes at a dilution of 1 part per million, whilst with a sample of cascara a concentration of 100 times as much was necessary. There was not much likelihood of mistaking cascara, senna or rhubarb for aloes.

Regarding various other extracts mentioned, he could not say what the result of tests on this would be—they had been dealing with aloes, B.P. He wished to emphasise the fact that, after 60 hours, reaction had been obtained for unhydrolysed, not for hydrolysed, aloes, as mentioned by Mr. Sage. The Bornträger reaction for hydrolysed aloes was not capable of giving a reaction for much less than 1 mgrm. in 10 ml., whilst, as already stated, the modified Schoutelen test (unhydrolysed aloes) gave a positive reaction with 0·01 mgrm. in that volume.

The Effect of Certain Salts on Fermentation in Dough

By R. H. CALLOW, M.Sc., A.I.C.

(Read at the Meeting of the North of England Section, December 2, 1933)

Bread is defined in this country in the Bread Acts of 1822 and 1836, but the Acts and the definition are practically a dead letter. Nobody puts into bread oats, buckwheat, Indian corn, peas, or rice, and it is the general practice of those engaged in the trade to add unpermitted ingredients, such as fat, sugar, fruit, chemical improvers, and bleaching agents. A Departmental Committee was appointed in 1923 to consider the addition of chemicals to flour, and published its findings in 1927. The findings are rather indefinite, and, in spite of the fact that the Committee viewed the use of certain chemicals unfavourably, the use of these has increased considerably since the Report was published.

Additions are made to bread for various purposes, and it is, of course, immaterial whether the additions are made by the miller or the baker. Some additions are made in order to alter the colour, the action in this case generally resolving itself into the bleaching of carotene. Some are added to strengthen or weaken the gluten, some to increase the diastatic power. Other substances increase water absorption, some act as yeast foods and activators, and a number of obviously harmless substances are added to improve flavour or nutritive value.

Certain improvers and yeast foods have been known and used for a long time, as, for example, sugar, fat, milk, malt, potatoes, etc., and it has been known for an equally long time that the use of some of these is attended with a certain amount of risk; thus, the use of a large quantity of malt may give a good flavour, but the production of dextrins and the hydrolysis of the proteins will ruin the bread. Also, potato is a very good yeast food, but one is very likely to get the bread infected with "rope" by its use.

Before considering the effect of certain salts on fermentation in dough it may not be out of place to mention some of the main changes taking place during fermentation and baking. There is a certain amount of fermentable sugar in flour, and, when a dough is made, further sugar is formed by the action of wheat diastase on the starch. If no other sugar or diastatic substance is added, this is the total supply of sugar that is available for the yeast, but often cane sugar or malt extract is added to make up for deficiencies in original sugar or diastase. At the beginning of the dough-stage fermentation is slow, and diastatic action is normal, and, therefore, the sugar-content increases. The fermentation, however, increases continuously in speed, owing to the activation and growth of the yeast, and thus there may come a time when the rate of consumption of sugar by the yeast is equal to the rate of production of sugar by diastase. After this point the rate of fermentation still increases, resulting in a diminishing sugar-content until a shortage of sugar is indicated and the rate of increase of gas-production falls off. Eventually the rate of gas production becomes steady, and then begins to fall.

In order to produce a good bold loaf with a pleasing aspect, it is essential that when the dough goes into the oven the rate of gas production should be vigorous, although not violent, but it must not be falling, otherwise the bread does not spring in the oven, and may actually shrink during the baking process.

The other main change that takes place is in the physical condition of the gluten. When the dough is first made it will not stretch much without breaking. It is said to be short-textured, and this shortness or lack of extensibility is due to the tough condition of the gluten. During fermentation the p_H of the dough decreases, owing to saturation with carbon dioxide and the production of a certain amount of lactic and, possibly, other acids, the gluten becomes more dispersed, and the dough becomes softer and more extensible, and yields more easily to pressure or tension. Also, the proteolytic enzymes in the flour act in the same direction. This softening of the gluten, making it easily extensible, is referred to in trade circles as the "maturing" of the gluten. If it goes too far, it is called the "breaking down" of the gluten, but both are essentially the same thing.

When the dough is placed in the oven there is a rapid production of gas, owing to two causes. First, the dough is saturated with carbon dioxide, which is liberated during heating; secondly, the yeast acts more rapidly as the temperature rises to the optimum. It is essential for the production of a good loaf that the gluten should be sufficiently matured to give way and expand under the pressure of the rapidly developed carbon dioxide, but not so matured as to collapse. If the dough is insufficiently matured, it will be too tough and will tear in the oven, giving a rough unsightly loaf. If, on the other hand, it is over-matured, the strength goes out of the gluten and the resulting loaf is very crumbly. These two points may not affect the nutritional value of the loaf, but they do count with the public.

Fermentation in dough is always accompanied by a loss of flour solids. Where the dough is made of flour, yeast, salt and water this loss is from 2·5 to 3 per cent. in processes of about 3 to 5 hours' duration. In long-process doughs some authors report losses as high as 11 per cent., but this cannot be considered as commercial practice. The highest losses commercially obtained are probably in the neighbourhood of 5 to 6 per cent. of the total weight of flour and sugar. This loss was generally regarded as a necessary evil. The yeast does the work and demands its price. This view was accepted until about 1915, when Swanson and Willard,[1] and Kohman, Hoffman[2,3] and others carried out a series of experiments on the nutritional requirements of yeast.

It had long been known that yeast required sugar, nitrogenous matter, phosphates and potash, and it was known in the brewing trade that water containing fairly large quantities of calcium gave a faster fermentation and made better beer than soft waters.

The work of Kohman, Hoffman and others was, in the first instance, an attempt to discover why bread made in several bakeries belonging to the one firm, each using the same raw materials, process, formula, and plant, varied considerably in quality, volume, and general characteristics. Suspicion eventually fell on the water supplied, and analysis of the water showed large differences in calcium-content. In those bakeries working on a soft-water supply the fermentation was sluggish, whereas in those working on hard water the fermentation was relatively fast. When the waters were treated so as to equalise the calcium differences, the differences in the products of the bakeries disappeared, and the bread was standardised. Gas-production tests showed, however, that if the calcium-content was still further increased, the activity of the yeast was increased. Different calcium salts activate the yeast to different extents, as the anion may have a specific effect as well as the cation. Also, the acid salts will have an accelerating effect in respect of the acidity.

Practically all except calcium compounds show an activating effect on yeast, those having an alkaline reaction, *e.g.* carbonate and bicarbonate, hydroxide, and normal phosphate, also those salts in which the anion has an antiseptic or preservative action, *e.g.* benzoate, sulphite, etc. The activation by the addition of calcium salts is, to all intents and purposes, immediate, but the effect on gas-production is relatively larger with a weak yeast than with a strong yeast. The following figures indicate the ml. of gas evolved in 5 hours from doughs made from 56 grms. of flour, 33 grms. of water, 0·8 grm. of salt, and 0·5 grm. of yeast at a temperature of 80° F., without, and with, the addition of 0·075 grm. of calcium sulphate.

	Control	Calcium sulphate	Percentage increase
1.	304	330	8·2
2.	272	298	9·5
3.	240	271	12·9

Somewhat similar figures are obtained with other calcium salts when the acid radicle has no specific effect. It will be seen, therefore, that the tendency of the addition of calcium salts is to standardise the gas-producing power of yeast in dough.

In addition to stimulating gas-production, calcium salts have an effect on the gluten of dough, by which the gas-retaining powers are increased. Thus, of two doughs showing the same rate of gas-formation in the oven, that containing added calcium salt will give a larger loaf than the one without such addition. Certain results obtained by Hoffman[3, 4] indicate that addition of a calcium salt to dough increases the rate of reproduction of the yeast. Yeast cells in dough are difficult to count, and the technique, even under the best conditions, must be somewhat crude, but the fact that Hoffman always obtained an increased effect lends weight to the results. An an example, the increase found in a dough after six hours was 45·1 per cent., whereas in a similar dough containing calcium sulphate (0·125 per cent. on the flour) the increase in yeast count was 57·6 per cent.

The activity of yeast in dough is only slightly influenced by additions of potassium compounds and phosphate, owing, presumably, to the relatively large quantities of these already present in flour.

The nitrogenous requirements of yeast are normally derived from the proteins and similar bodies in the flour, and thus during fermentation there is a partial destruction of protein, resulting in a reduced amount available for gluten formation. It has been found that if nitrogen is supplied in a more readily assimilable form, the activity of the yeast is increased. Thus if glutamic acid, prepared by hydrolysis of gluten with hydrochloric acid, or peptone, is added to a dough, gas-production is considerably increased. It was found by Willard and Swanson that a still simpler nitrogenous body, namely, ammonium chloride, would increase the activity of yeast, but that ammonium phosphate was ineffective, and ammonium tartrate and acetate were detrimental. There appears to have been some fault in the technique, as we and others have tried several ammonium salts and found them all effective, except the alkaline salts.

One feature of the activation of yeast by the addition of ammonium salts, which is quite different from the activation by calcium salts, is that, whereas calcium activates, practically immediately, the action of ammonium salts is delayed for some time and then takes place rapidly. For the first three hours ammonium chloride has practically no effect on gas-production in dough, but the subsequent effect is considerable. Ammonium salts activate all types of baker's yeast, *i.e.* strong or weak, old or new, and, as with calcium salts, the relative effect is more marked with the weaker yeasts. The following figures refer to doughs similar to those in the former series, but containing 0·03 grm. of ammonium chloride instead of 0·075 grm. of calcium sulphate:

	Control ml.	Ammonium chloride ml.	Percentage increase
1	300	325	8·3
2	281	307	9·25
3	278	310	11·5

In these tests the gas-productions have been given up to the time when such a dough would normally be set in the oven.

It does not by any means follow that if two substances will activate an organism, both together will doubly activate it. There is generally a limit to what the organism can do. With calcium and ammonium salts, however, the activating action is cumulative. For example, a set of doughs was made somewhat similar to those previously mentioned but containing 0·425 grm. of yeast instead of 0·5 grm., and also containing 0·03 grm. of ammonium chloride. To one was added, in addition, 0·075 grm. of calcium sulphate. The average gas-productions after 5 hours were

1.	Without calcium sulphate ..	262 ml.
2.	With calcium sulphate ..	285·5 ml.
	Percentage increase ..	8·97

It has already been pointed out that when the dough goes to the oven a vigorous gas-production (but not a violent one) is necessary, as otherwise the loaf will not expand rapidly enough to accommodate the gas production. It is, therefore, necessary, if the yeast is highly activated, to reduce the quantity of yeast used. Curves of the hourly rates of gas-production in doughs containing (i) no additions; (ii) 0·03 grm. of ammonium chloride and 15 per cent. less of yeast; (iii) 0·03 grm. of ammonium chloride plus 0·075 grm. of calcium sulphate and 15 per cent. less of yeast; (iv) 0·03 grm. of ammonium chloride plus 0·075 grm. of calcium sulphate, and 25 per cent. less of yeast have been constructed.

These show that the control dough has the more rapid gas-production in the early stages, but that the dough containing ammonium chloride with a 15 per cent. yeast reduction passes it between the fourth and fifth hours. As, in the final stages of bread-making, it is the rate of gas-production that is important, the use of these salts leads to a considerable economy in yeast.

Another point is worthy of consideration. The control curve cuts the curve with ammonium and calcium salts and 25 per cent. yeast reduction at 4·1 hours. By this time the control dough had developed 216 ml. of gas, whereas the treated dough had developed only 178 ml. Further, the rate of gas-production in the control dough is falling slowly, whilst that in the treated dough is rising rapidly. A dough of this composition should go to the oven at about 4½ hours, and it will be seen that to bring the rates of fermentation to the same value at this point, the yeast would have to be still further reduced, thus further reducing the total gas-production in the treated dough. As it is, the losses in the treated dough are roughly 82 to 83 per cent. of those in the control dough at the time when the rates of gas-production are equal, and, taking the average losses during fermentation as 3 per cent., this will give 0·5 per cent. conservation of carbohydrate.

The rate of gas-production, however, is not the only factor. Two other very important factors are the rate of gluten maturing, and the gas-retaining capacity of the dough. Without dealing in detail with maturation of gluten it suffices to say that traces of potassium bromate and iodate influence to a remarkable extent the elastic properties of gluten in the same direction as yeast fermentation, and that, therefore, by the use of a small quantity of potassium bromate (*e.g.* 0·001 per cent. by weight of the flour), the amount of fermentation required to ripen the gluten satisfactorily is very considerably reduced.

It has been mentioned that a strong gas-production is necessary in the final stages. This is really an incomplete statement. Actually the rate of gas-production should be considerably higher than the rate of loss of gas from the dough. Under these conditions the loaf will rise well in the oven and make a good loaf; otherwise it will not. If the gas-retaining power of the dough can be increased, thus reducing the rate of loss of gas, the rate of gas-production may be correspondingly reduced. Both calcium salts and salts of bromic and iodic acids act in this way, and thus a further conservation of carbohydrate becomes possible. Actually, we find in large-scale tests that, by the addition of 0·25 lb. of calcium sulphate ($CaSO_4,2H_2O$), 0·1 lb. of ammonium chloride and 0·003 lb. of potassium bromate to a dough made from 280 lbs. of flour, the fermentation losses are reduced by at least 50 per cent.

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The Investigation of Japanese Beeswax (III)

Composition of Hydroxy Fatty Acid

By HARUICHI IKUTA

(*Read at the Meeting, October* 4, 1933)

LIPP and Kovács (*J. prakt. Chem.*, 1919, 99, 243) claimed to have isolated hydroxymargaric acid (m.pt. 58° C.) and *iso*-hydroxymargaric acid (m.pt. 71°–72° C.) from East Indian beeswax, but in my second paper (ANALYST, 1933, 58, 635) I have shown that this so-called "hydroxymargaric" acid is a mixture. There is, however, a hydroxy fatty acid present, partly in the free and partly in the combined state, in Japanese beeswax, and the investigation of its characteristics is the subject of the present investigation.

The wax used was of undoubted purity, having the characteristics previously described for Japanese beeswax (ANALYST, 1931, 56, 430). The mixed fatty acids (about 180 grms. of m.pt. 48·5°–49° C.; neutralisation value, 190·5) were converted into their ethyl esters and fractionally distilled at reduced pressure (2 mm.). The ethyl ester (51 grms.) of b.pt. 180°–200° C. at 2 mm. was then acetylated and again distilled *in vacuo*, the following fractions being obtained:

Fraction No.	B.pt. °C.	Pressure mm.	Yield Grms.	Saponification value	M.pt. or behaviour at 0° C.
1.	below 175	1·5	11	224·6	Rapidly solidified
2.	180	,,	12	241·9	Slowly solidified
3.	185		8	262·4	Almost liquid
4.	190		10	277·8	Liquid
5.	192		8	287·6	Liquid
6.	196		2	277·4	Almost liquid
7.	200		2	251·8	42°–42·4° C.
8. (Residue)		—	2	213·6	42°–42·6° C.

Formula	Acetyl-ethyl ester	Saponification value
$C_{16}H_{32}O_3$	$C_{15}H_{30}(O.CO.CH_3)COOC_2H_5$	318·5
$C_{17}H_{34}O_3$	$C_{16}H_{32}(O.CO.CH_3)COOC_2H_5$	306·8

The mixed fatty acids obtained by saponification of fractions 3, 4, 5, and 6 were viscid solid masses, with m.pts. 46°–48° C. and neutralisation values of 188–192. The crude reputed hydroxy acids were separated from the other fatty acids by means of their insolubility in petroleum spirit (b.pt. 40°–60° C.) and ligroin (b.pt. 85°–120° C.).

After three crystallisations from the former solvent, and seven from the latter, white lustrous needle-shaped crystals (m.pt. 69°–69·3° C.) were eventually obtained, and a further yield of powdery crystals (m.pt. 69·2°–69·4° C.) was separated from the mother-liquor from the second and third petroleum spirit crystallisations. The filtrate from the first petroleum spirit crystallisation yielded a liquid fatty acid and a solid fatty acid melting at 53°–54° C.

The crystals from the second and third crystallisations (m.pt. 57°–58° C.) were recrystallised four times from petroleum spirit and then gave a product agreeing approximately in its values with Lipp and Kovács' hydroxymargaric acid (m.pt. 57°–58° C.; neutralisation value, 196·3, and acetyl value 172·1), but the elementary analysis did not agree with the formula $C_{17}H_{34}O_3$. The substance was, therefore, fractionally precipitated with barium acetate from 95 per cent. alcohol, and the seventh fraction yielded a fatty acid melting at 67·8°–68·1° C., and with neutralisation value of 201·7. Fractional crystallisation from petroleum spirit also yielded a final fraction containing a fatty acid melting at 62·1°–62·2° C.

Hence the so-called "hydroxymargaric" acid probably consists of a mixture of $C_{16}H_{32}O_3$ and $C_{18}H_{36}O_3$, or some other higher fatty acid.

The crude hydroxy acid (m.pt. 69·2°–69·4° C.), apparently corresponding with Lipp and Kovács' *iso*-hydroxymargaric acid, also had an elementary composition corresponding with a mixture of C_{16} and C_{18} hydroxy acids. When fractionally recrystallised from ligroin (b.pt. 85°–100° C.) it yielded in the fourth to the ninth fractions a fatty acid melting at 70°–70·7° C., whilst the residue contained an acid melting at 63·3°–63·8° C. Fractional precipitation with barium acetate also effected a separation of the crystals into two components.

Further re-crystallisation of the apparent *iso*-hydroxymargaric acid from ligroin yielded at the 28th crystallisation a nearly pure chemical substance (judging by the differences between the m.pts. of the crystals and of the residues in the mother liquors).

The analytical values of this new hydroxy fatty acid were as follows:—M.pt., 73·8°–74·2° C.; neutralisation value, 205·8; acetyl value, 178·3; m.pt. of acetylated acid, 39·3°–39·8° C.; saponification value of acetylated acid, 356·6. The calculated values for $C_{16}H_{32}O_3$ are: Neutralisation value, 206·1; acetyl value, 178·5; saponification value of acetylated acid, 357·0.

The name "hydroxypalmitic" acid is provisionally suggested for the new acid, which constitutes about 20 per cent. of the mixed fatty acids in the wax. It is a hard viscid mass, readily soluble at the ordinary temperature in methyl and ethyl alcohols, acetone, benzene, chloroform, and ethyl acetate. In particular, it dissolves rapidly in 60 per cent. alcohol, and does not separate from the solution at 0° C. It is slightly soluble in hot, but insoluble in cold petroleum spirit. When the hot solution is cooled to room temperature it yields white lustrous aggregates of needle-shaped crystals. The acetyl derivative is a viscous white substance crystallising from petroleum spirit in white powdery crystals.

I wish to thank Professor Ueno for his assistance in this work.

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The Determination of Traces of Bismuth in Presence of Other Metals

By L. A. HADDOCK, B.Sc., A.I.C.

In searching for a rapid and accurate method for separating bismuth from other metals, attention was drawn to the use of diphenylthiocarbazone by Allport and Skrimshire (ANALYST, 1932, 57, 440; *Quart. J. Pharm.*, 1932, 5, 461) for the isolation of lead from other metals. They state that bismuth, if present, is also extracted by a solution of the reagent in chloroform, but they have not investigated the matter from a quantitative standpoint. Experiments in this direction show that, under the conditions outlined by Allport and Skrimshire, amounts up to 1 mgrm. of lead, bismuth and thallium could be quantitatively isolated from other metals. Possibly, still larger amounts might be extracted similarly. In the case of bismuth, quantities of 10 to 100γ were entirely extracted from 1 grm. of silver, iron, copper, mercury, etc. This extraction method is obviously a marked improvement on methods involving precipitations, since losses due to adsorption or incomplete precipitation cannot occur.

The next stage of the investigation involved the colorimetric determination of the bismuth. Several colorimetric methods have been proposed, one of the oldest of which is based on the yellow colour of the iodobismuthite ion. Frick and Engemann (*Chem.-Ztg.*, 1929, 53, 505) show that the colour is proportional to the bismuth concentration, whilst, amongst other workers, Portnov and Skvorzov (*Farm. Zhur.*, 1928, 534; *Brit. Chem. Abst.*, 1930, 184A) obtain a sensitivity of 2·5γ of bismuth per ml. by this method.

Aubrey (*J. Pharm. Chim.*, 1922, 25, 15) finds that the orange-red precipitate of quinine iodobismuthite enables approximately 1·25γ of bismuth per ml. to be determined. Cuny and Poirot (*id.*, 1923, 28, 215) use gum arabic as a stabiliser in this method, and Laporte (*id.*, 1923, 28, 304) prevents the actual precipitation of iodobismuthite by the addition of acetone.

Girard and Fourneau (*Compt. rend.*, 1925, 181, 610) found that, of all the synthetic bases examined by them, tetra-cetylammonium hydroxide yielded the most intensely coloured iodobismuthite. The coloured substance could be extracted by several organic solvents and was sensitive to 0·25γ of bismuth per ml. Several other metals also yielded coloured complexes in a similar manner.

Thiourea produces a yellow colour with bismuth salts in acid solution, as described by Sensi and Seghezzo (*Ann. Chim. appl. Roma*, 1929, 19, 392). Small amounts of most other metals do not interfere, but they may tend to produce precipitates. The colour is sensitive to 10γ of bismuth per ml., but is largely dependent on the quantity of reagent added, and is thus not entirely suitable for quantitative work.

The reagent of Girard and Fourneau (*loc. cit.*) would be very suitable for the determination of the bismuth isolated by chloroform extraction. It must, however, be prepared in the laboratory, as it is not generally available, and, for this and other reasons, attention was again directed to the classic iodobismuthite method. It was discovered that the free iodobismuthous acid, presumably formed by the action of soluble iodides added to an acid solution of a bismuth salt, was soluble in several organic solvents, usually esters and higher alcohols, and could be extracted from the aqueous solution. Amyl alcohol was a good solvent, but was somewhat too viscous for use alone. Ethyl acetate was also useful, but the solubility in aqueous solution (about 9 per cent. at room temperature) was a disadvantage. Ultimately, after many trials, a mixture of three parts of amyl alcohol and one part of ethyl acetate was used as the extracting solvent, as it was less viscous than the pure amyl alcohol. Powell (ANALYST, **1933**, **58**, 706), working independently, also devised a similar procedure for bismuth. The method is very useful for the direct determination of minute amounts of bismuth in the presence of considerable quantities of highly coloured ions, such as those of chromium, nickel or cobalt. The yellow bismuth compound is readily extracted from these solutions, and, by then adding a known quantity of a standard bismuth solution to the aqueous solution and extracting again, it is possible to be certain that both standard and unknown are examined under identical conditions of acidity and presence of other ions.

Several experimental difficulties were encountered when the process was examined from a quantitative standpoint. Since traces of liberated iodine would seriously interfere in matching the colour, excess of sulphurous acid was added to overcome this difficulty. It was found that the solutions became bright yellow even in complete absence of bismuth, and this yellow substance could itself be extracted by the solvent. The yellow compound is possibly an iodosulphinic acid, $I(HSO_2)$, as suggested by Péchard (*Compt. rend.*, 1900, **130**, 1188). The use of small quantities of hypophosphorous acid was tried, but the reaction was insufficient under those conditions. Finally, a very slight excess of sulphurous acid was added, followed by a few ml. of approximately 30 per cent. hypophosphorous acid solution to prevent any slow liberation of iodine. Under these conditions bismuth-free solutions remained colourless. Solutions containing about 50 per cent. of concentrated hydrochloric or sulphuric acid gave yellow complex iodo acids, and it was found that the upper limit of acidity to obtain a colourless blank was about normal. Hydrochloric acid and chlorides had a very marked bleaching action on the bismuth colour, but sulphuric acid had little effect. This acid was, therefore, used in all the determinations. Free phosphoric acid did not have a very marked effect on the colour, but a considerable excess of the acid (a 40 per cent. solution), tended to produce a yellow compound with potassium iodide.

METHOD.—The isolation of the bismuth prior to its determination is, of course, only necessary with certain interfering metals. It may, however, also be useful in those cases in which, while not actively interfering, the metal renders the direct test for bismuth less sensitive, as does arsenic or cadmium, for instance.

Organic matter should be destroyed by wet oxidation, since ignition invariably leads to loss of bismuth. Bohet (*J. Pharm. Belg.*, 1929, **2**, 805) finds that calcination in presence of halides may cause a loss of 50 per cent. of the metal. The best method is oxidation with concentrated sulphuric acid and 30 per cent. hydrogen peroxide. Metals or alloys may be dissolved in an appropriate acid or mixture of acids, excess of which is removed by gentle evaporation. Metallic salts are dissolved in water without general preliminary treatment. The neutral or acid solution is transferred to a separator and 2 grms. of citric acid are added. When relatively large amounts of iron salts are present, 10 grms. of citric acid may conveniently be used. Ammonia (sp.gr. 0·880) is introduced until the liquid is almost neutral to litmus, and at this stage the liquid must be continually cooled under running water. Ten ml. of approximately 10 per cent. ammonia (which should make the reaction alkaline) and 2 grms. of potassium cyanide are added, but, when large quantities of copper, silver, etc., are present, the amount of potassium cyanide should be increased to 5 or 10 grms. The cold solution is then shaken vigorously with four portions of 15 ml. each of a 0·1 per cent. solution of diphenylthiocarbazone in chloroform. Each chloroform extract is washed with 10 ml. of water contained in another separator, and the extract is transferred to a 100-ml. pyrex Kjeldahl flask. The chloroform is evaporated, and 1 ml. of concentrated sulphuric acid is added. The acid is carefully heated over a micro-burner and 30 per cent. hydrogen peroxide is added, drop by drop, until all the organic matter has been destroyed. The acid solution is transferred to a separator with 20 ml. of water and well cooled. Very dilute iodine solution is added, drop by drop, to destroy the excess of sulphur dioxide often produced from the acid. If this is not done, entirely erroneous results may sometimes follow, owing to the formation of the yellow iodosulphinic acid. Four drops of approximately 5 per cent. sulphurous acid solution, 2 ml. of 30 per cent. hypophosphorous acid and 5 ml. of fresh 10 per cent. potassium iodide solution are then added. The liquid is well shaken with successive 3 ml.-quantity of a mixture of three parts of amyl alcohol and one part of ethyl acetate until the final extract is almost colourless. The extracts are all collected in a small graduated cylinder. A standard colour is prepared by adding a known amount of a 0·001 per cent. solution of bismuth to the aqueous solution and again extracting with the organic solvent as before. Several other standards may be similarly prepared. Each of the series of extracts is adjusted to the same volume (about 6 ml. for 10 to 40γ of bismuth and 10 to 12 ml. for 40 to 100γ). After filtration through minute plugs of cotton wool they are ready for comparison.

NOTES ON THE METHOD.—For quantities of bismuth less than 20γ direct visual comparison in 10-ml. Nessler tubes readily gave results of an accuracy equal to that given by a colorimeter. For larger quantities a colorimeter of the Duboscq type was used. The total amount of aqueous solution containing the bismuth should not exceed 40 ml. In general, two extractions will remove about 5 to 20γ of bismuth, four extractions, 50 to 80γ, and five must be used for 100γ.

EXPERIMENTAL.—The standard bismuth solution was prepared from pure bismuth oxychloride. This was prepared as follows:—Bismuth carbonate of commerce was gently ignited to oxide. The oxide was dissolved in the minimum excess of (A.R.) hydrochloric acid, a large excess of water was added to the solution, and the precipitated oxychloride was washed several times by decantation, then dissolved in hydrochloric acid and re-precipitated by the addition of water. It was thoroughly washed with water and finally dried for several hours at 300° C.

in an electric oven until constant in weight. It was preserved in the dark. Assayed as bismuth phosphate, it showed 99·98 per cent. of bismuth oxychloride.

A 0·1 per cent. solution of bismuth was made from this compound, the minimum excess of hydrochloric acid to effect complete solution being used. The dilute solution (0·001 per cent.) was prepared as required by diluting 10 ml. of the strong solution to a litre, a little dilute hydrochloric acid being used to prevent any precipitation. One ml. of this solution contained 10γ of bismuth.

It was shown that, for small differences in bismuth-content, Beer's Law was valid for the amyl alcohol solution of the iodobismuthous acid. Two known quantities of bismuth were extracted as described, and the extracts were transferred to the cups of the colorimeter. It will be seen from the following results that the ratio of the quantities of bismuth is equal to the inverse ratio of the heights of the liquid. This has already been proved to be true for aqueous solutions of the acid by Frick and Engemann (*loc. cit.*).

Bismuth in γ	Ratio	Colorimeter reading	Inverse ratio of colorimeter reading
10	0·500	20·3	0·492
20		10·0	
50	0·833	20·0	0·830
60		16·6	
100	0·909	15·0	0·907
110		13·6	

APPLICATION IN PRESENCE OF INTERFERING METALS.—Interfering metals in this determination are primarily those which themselves react with soluble iodides. The complete process of chloroform extraction prior to the determination must always be used when they are present, either alone or in mixtures. Autenrieth and Meyer (*loc. cit.*) found that mercury does not interfere if excess potassium iodide is used, owing to the formation of the stable salt K_2HgI_4. This may be true for small amounts of mercury, but it was found that quantities of the order of 1 grm. produced a brilliant yellow complex body under these conditions, and that this compound also was extracted by the amyl alcohol; antimonious salts with a large excess of iodide reacted similarly. Arsenious salts produced no colour, but large quantities had a marked effect in lowering the sensitivity of the bismuth test. Large quantities of arsenic in the tervalent state, however, may be removed by repeated evaporation with hydrochloric acid.

One grm. of cadmium, present as sulphate, had little bleaching action under the conditions proposed, but 5 grms. of cadmium sulphate had a marked bleaching effect. This could be largely overcome by employing more potassium iodide.

Stannic tin had little bleaching effect, but stannous tin interfered. For large quantities of tin it is better to extract the bismuth with diphenylthiocarbazone before proceeding to the colorimetric determination.

Didymium nitrate was selected as a typical rare-earth mixture. It was also found to exert a marked effect in reducing the sensitivity of the bismuth test, so that a chloroform extraction seems to be indicated when quantities of rare-earth metals greater than about 1 grm. are present. The following results, in which the bismuth was extracted prior to its determination, are typical:

Metal	Quantity in grms.	Bismuth added in γ	Bismuth found in γ
Antimony ..	1	30	33
Copper	1	20	18
Copper	1	90	93
"Didymium" ..	2	10	12
Iron (ferric) ..	1	10	12·8
Mercury ..	1	50	50
Silver	1	20	20
Silver	1	100	114
Tin (stannic) ..	1	20	17·5

APPLICATION IN PRESENCE OF NON-INTERFERING METALS.—It was found that the bismuth could be determined directly in the presence of considerable quantities of alkali metals, alkaline earth metals, magnesium, manganese, zinc, cobalt, chromium, aluminium, cadmium, thorium, zirconium and titanium. Large quantities of zirconium and titanium (of the order 2 grms.) did, however, tend to reduce the sensitivity of the test for quantities of bismuth less than 30γ. When highly-coloured ions, such as those of cobalt, nickel and chromium, were present in the aqueous solution at concentrations of 1 grm. in 40 ml., control determinations showed that a very small amount of the coloured compound was extracted by the organic solvent, owing to the slight solubility therein of the aqueous solution. By the addition of the standard bismuth solution to this aqueous solution, it is, of course, obvious that both the standard and unknown organic extracts will be tinted to exactly the same extent—a matter of some importance when small amounts of bismuth are being determined. In any case, the amount of colour extracted is very feeble, and as little as 10γ of bismuth, if present, is easily visible.

Mention has been made before of the bleaching effect of hydrochloric acid. Large quantities (5 grms.) of ammonium fluoride and sodium chloride similarly rendered 20γ of bismuth only just visible. Preliminary "fuming" with sulphuric acid is needed in these cases. Large quantities of neutral sulphates (5 grms.) and, to a less extent, of phosphates, tended to impart a persistent very faint yellow colour to the organic solvent. The colour was negligible, however, and 10γ of bismuth were easily recognised in its presence. It would be automatically compensated by the procedure previously described.

Typical results for metals showing little interference are given below:

Substance	Quantity in grm.	Bismuth added in γ	Bismuth found in γ	Remarks
Cobalt	1	10	11	Colour of extract easily visible
Cobalt	1	40	43	
Nickel	1	10	12	Do.
Nickel	1	40	42·5	Very faint yellow on blank
Manganese ..	1	10	9·5	Blank; very faint yellow
Manganese ..	1	40	41	
Chromium ..	1	10	12·5	Do.
Chromium ..	1	40	42	
Cadmium ..	1	10	9·5	Little bleaching noticed
Zinc	1	10	10	

Some effects of acidic radicles are noted below:

Substance	Quantity in grms.	Bismuth added in γ	Remarks
Potassium sulphate ..	5	10	Bismuth colour easily visible. Blank: faintly yellow
Sodium chloride ..	5	10	Colour scarcely visible
Sodium chloride ..	5	20	Colour just visible
Ammonium nitrate ..	5	10	Colour easily visible
Magnesium sulphate ..	5	10	Do.
Barium chloride ..	3	10	Colour fairly easily visible; used dil. HCl
Strontium chloride ..	3	10	Do.
Calcium phosphate ..	3	10	Used a minimum of dilute HCl. Colour easily visible

Vanadates gave a yellow colour with mineral acid, but had little effect on the test for bismuth. Molybdates tended to give a blue colour in the aqueous menstruum, but the coloured bismuth compound could still be extracted without interference. Tungstates did not interfere if phosphoric acid was present to keep the tungstic acid in solution. Uranium (as uranyl salt) also did not interfere.

SUMMARY.—A method has been described for determining 5 to 100γ of bismuth in the presence of quantities of at least 1 grm. of most other elements. The only two elements interfering seriously with the method are lead and thallium in quantities greater than about 0·5 mgrm.

I wish to thank Dr. A. M. Ward for his interest in this work.

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Equalisation of Temperature in Electric Ovens

BY F. G. H. TATE, F.I.C.

(*Read at the Meeting, February* 7, 1934)

THE maintenance of a uniform temperature in ovens used for the determination of moisture in tobacco is of special importance, owing to the fact that a temperature of 212° Fahr. is prescribed in one of the Tobacco Acts as that at which the tobacco must be dried.

Ovens heated by steam, although not very convenient, present little difficulty. A valve capable of barometric adjustment, if fitted to the boiler, ensures a supply of steam at satisfactory temperature, whilst equality of temperature throughout the drying chamber is promoted by the provision of tubular shelves through which the steam can circulate.

The necessity for increasing our oven capacity led to an investigation into the possibilities of electrical heating. An oven was obtained from a well-known firm of electric oven makers. Its approximate internal measurements are:—Width, 15½″; height, 14″; depth, 10″. The temperature-control consists of a capsule containing a liquid, whose thermal expansion and contraction, resulting in corresponding variation in the volume of the capsule, regulate a short lever which alternately connects or disconnects platinum points and makes or breaks the heating current. Heating elements are placed at the sides, top and bottom of the chamber. The shelves originally supplied consisted of perforated metal plates supported by brackets directly attached to the sides of the chamber. In the original arrangement of the oven the temperature was indicated by a thermometer inserted in the top left corner near the capsule, in such a manner that the portion of the scale with which we were concerned was outside the oven. For the purpose of our test we used, in addition to this, a number of maximum temperature thermometers which were afterwards replaced by a six-point electric recorder supplied by the Foster Instrument Company.

The oven was tested when empty, and also when fully loaded with samples. Under various conditions of loading it was found that pockets of hot air formed in the corners of the oven. As this postulated want of circulation of air, false sides were fitted into the chamber, the shelf brackets being fixed to these, and the plate shelves were replaced by others of the grid type. These measures failed to remove the inequalities of temperature, and consideration was given to the use of some form of fan which would ensure circulation.

A fan revolving horizontally in the top of the drying chamber was first tried. The top shelf, when loaded with samples, acted as a complete baffle, and this device proved entirely ineffective. After considerable further experiment the following arrangement was adopted :

The packing was removed from the door, the space between the inner and outer panels forming a chamber in which the fan is placed. The inner panel is cut as shown in the figure. The fan has four blades extended with flanges which, when the fan is in position, almost touch the front panel. A small subsidiary fan, attached to a spindle, extends into the centre of the oven. The fan is revolved at about 1200 revolutions per minute by means of a $\frac{1}{20}$ h.p. motor under the front of the oven, a double-spring belt being used for the purpose. The air is drawn from the centre of the oven, thrown into the corners of the fan chamber and then ejected through the triangular corner openings into the corners of the drying chamber. This effectively eliminates the thermal inequalities. The record from the Foster recorder shows the temperature at five points (four corners and the centre) of the oven fully loaded with samples throughout a run of seventeen hours. From 5 p.m. till 1 a.m. the fan was revolving, and the maximum difference covering the five points was less than one degree. At 1 a.m. the fan was switched off, and there was immediately inequality, the difference at times being as much as 20 degrees. At 6.45 a.m. the fan was re-started, and within about 45 minutes uniformity was re-established and maintained until the test was stopped at 10 a.m. This is typical of many similar runs.

In conclusion I would emphasise two points:—We have carried out this investigation solely in connection with tobacco, and we have no information as to the suitability of the method for other commodities.

We do not consider that we have yet reached finality. Several points still remain for investigation and experiments are proceeding.

I desire to thank Mr. W. J. Crispin for his assistance in this investigation, and the Government Chemist, Sir Robert Robertson, K.B.E., F.R.S., for permission to publish this note.

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Notes

The Editor wishes to point out that the pages of the Journal are open for the inclusion of short notes dealing with analytical practice and kindred matters. Such notes are submitted to the Publication Committee in the usual manner.

NOTE ON NITRATES IN MILK

(*Read at the Meeting of the North of England Section, December* 2, 1933)

The presence of nitrates in milk is usually taken as an indication of added water; a positive diphenylamine reaction in "appeal-to-the-cow" samples has occasionally been obtained, and no adequate explanation has been forthcoming. Wood (Analyst, 1932, **57**, 375) drew attention to the practice of adding saltpetre to milk from cows fed on turnips, and in an earlier note (Analyst, 1931, **56**, 248) he reported the absence of the secretion of nitrates in the milk of cows drenched with saltpetre, which, however, is in contradiction to Richmond's earlier observations (Analyst, 1893, **18**, 279).

It is well known that the diphenylamine reaction is not specific for nitrates. Many substances of an oxidising nature, such as hydrogen peroxide and hypochlorites, will also give positive reactions. It may not be generally known that disinfectants of the hypochlorite class are being recommended by manufacturers for sterilising dairy utensils, and it was thought advisable to direct attention to this point as offering another explanation, other than the addition of water, of the origin of the positive reactions for nitrate. A few experiments showing the delicacy of the diphenylamine and diphenylbenzidine reactions towards hypochlorite have been carried out, and the results are reported in this note.

A well-known disinfectant of the hypochlorite class contains approximately 1 per cent. of sodium hypochlorite in 17 per cent. brine solution. The literature issued by the manufacturers, describing its use in dairies, includes directions for cleaning milking machines and separators with a 1 in 100 dilution and refrigerators and other implements with a 1 in 50 dilution; other directions for sterilising the hands of the milkers and washing the byres and floors are also given. Solutions containing amounts of chlorine varying from 1 in 5,000 to 1 in 10,000 are, therefore, used in cleansing materials with which the milk comes into contact, and if these are not thoroughly rinsed with water, some contamination of the milk may occur. As little as one part of the diluted solution in one thousand parts of milk would give a chlorine-content to the latter of one in five million to one in ten million, which is within the limits of detection by diphenylamine and diphenylbenzidine. The regulations governing the use of disinfectants in this way are as follows:—

MILK AND DAIRIES ORDER, 1926, PART V, PARAGRAPH 21.

> Every cowkeeper or dairyman shall cause all vessels (including the lids of such vessels) and appliances used or intended to be used by him for containing, measuring or stirring milk, or for any other purpose for which they may be brought into contact with milk, to be kept at all times in a state of thorough cleanliness.
>
> For this purpose—
>
> (i) Every vessel, lid and appliance shall be thoroughly washed as soon as may be after use, and shall be cleansed and scalded with boiling water or steam before it is used again.
>
> (ii) No oxidising or preservative agent shall be used in the cleansing of any vessel or appliance.
>
> (iii) Every such vessel, lid or appliance, when not in use shall be stored in a clean place and shall be protected from dust and dirt.
>
> (iv) No such vessel or appliance shall be used for containing, measuring or applying any process or treatment to any article other than milk or milk products:
>
> Provided that the requirements set out in paragraphs (i) and (ii) shall not apply to mechanical milkers and similar appliances used in milking which are efficiently cleansed so that all trace of any substance used in the cleansing is removed before they are brought into contact with milk.

The routine testing of milk for nitrates was advocated by Lerrigo (ANALYST, 1930, **55**, 433), and his technique was used in making these tests. Samples of milk which gave a negative diphenylamine reaction received the addition of the disinfectant so as to contain quantities of chlorine varying from one part in a thousand to one part in ten million. A positive result was given in all cases, the delicacy of the reaction and the depth of colour obtained being similar to those for the same amount of nitrates added to milk. One part per million was easily detected, one part in five or ten million just discernible. By using diphenylbenzidine, as advocated by Monier-Williams (ANALYST, 1931, **56**, 397) the delicacy was increased nearly tenfold. One in ten million of chlorine gave a good blue colour about equal in depth to that obtained from one in ten million of nitrate. The milks were allowed to stand for over a week until completely sour and then re-tested. No diminution in the colours obtained was noticed in any case.

It was thought of interest to see if a distinction between nitrates and hypochlorites could be made by means of the ortho-tolidine test, as used for estimating the chlorine requirements of bath water and sewage. The precautions and technique advocated by Lea (*Chem. and Ind.*, 1933, **52**, 245T) were taken, but in no case, even with as high a concentration as one in a thousand of chlorine in milk, was a positive reaction given. This is not altogether surprising, as this test is used for determining "chlorine requirement," and will give a colour only when this has been met and residual chlorine is present, and with milk the chlorine would be absorbed by the organic matter. The ortho-tolidine test is capable of detecting 1 part of chlorine in 100,000 in 1 ml., which is of the same order as the amount added to milk in these experiments.

How far the use of hypochlorite disinfectants is becoming general in dairies and how thorough the farmers are in rinsing the utensils is, of course, unknown, but it requires only a contamination of 1 part of the recommended diluted disinfectant to 1000 parts of milk to give a positive reaction, which might be reported as being due to the presence of nitrate.

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AN IMPROVED FORM OF SPRENGEL TUBE

The under-surface of the arms of the Sprengel tube is made of white enamel glass. This principle, which, for many years, has been applied to thermometers, has many advantages. Thus, the meniscus of the liquid in the arms is more clearly defined, increasing the ease and accuracy of its adjustment. Alterations in the volume of liquids with a high coefficient of expansion are avoided, as there is no need to remove the Sprengel tube from the water until the final adjustment has been made.

A. D. Gardiner

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Official Appointment

The Minister of Health has approved the appointment of

Thomas Reginald Hodgson as Public Analyst for the County Borough of Bury, in place of T. J. Hutchinson (deceased) (Feb. 17, 1934).

Notes from the Reports of Public Analysts

The Editor would be glad to receive the Annual or other Reports of Public Analysts containing matter of special interest to the Society. Notes made from such Reports would be submitted to the Publication Committee.

CITY OF BIRMINGHAM

Report of the City Analyst for the Fourth Quarter, 1933

Of the 1283 samples submitted by the inspectors during the quarter, 58 were bought formally and 1225 informally. Thirty-three samples of foods and 8 of drugs were found to be adulterated or incorrect.

Tea "Rich in Vitamins."—The label on a sample of tea described it as rich in vitamins and as being blended with the leaves of a tropical plant having remarkable curative properties in the case of certain diseases. The claim for vitamins was a pure invention, since, according to the latest information, black tea contains no vitamins, with the possible exception of a trace of vitamin *E*.

The packer was cautioned and agreed to omit the reference to vitamins.

The tropical plant was maté, or Paraguay tea, of which about 7 per cent. was present. This plant resembles tea and coffee in many of its properties, and particularly in its content of caffeine.

H. H. Bagnall

Legal Notes

Under this heading will be published notes on cases in which points of special legal or chemical interest arise. The Editor would be glad to receive particulars of such cases.

SCOPE OF RIGHTS IN A TRADE MARK

IRVING'S YEAST-VITE, LTD. *v.* HORSENAIL

ON February 1st the House of Lords dismissed the appeal of Irving's Yeast-Vite, Ltd. from the judgment of the Court of Appeal, which had affirmed the decision of Mr. Justice Bennett, who had held that the defendants had not infringed the appellants' registered trade mark "Yeast-Vite" by selling tablets, not of the appellants' manufacture, in bottles labelled: "Yeast Tablets, a substitute for Yeast-Vite."

The trade mark had been registered by the appellants in Part A, Class 3 of the Register, and they submitted that the effect of registration as proprietors of a trade mark in Part A was both to create and confer an exclusive right of property in that trade mark. The evidence on behalf of the appellants was to the effect that the respondents' tablets differed widely from Yeast-Vite in composition and were not in any true sense a substitute for it.

Both Mr. Justice Bennett and the Court of Appeal held themselves bound by *Edward Young & Co., Ltd.* v. *Grierson Oldham & Co.* They held that the respondent had not used the appellants' trade mark "as a trade mark," and that there had been no infringement of the right conferred by section 39 of the Trade Marks Act, 1905, according to which

> . . . the registration of a person as proprietor of a trade mark shall, if valid, give to such person the exclusive right to the use of such trade mark upon or in connection with the goods in respect of which it is registered. . . .

Lord Tomlin, in the course of his judgment, said that the question here was: What was the property right of the appellants and had it been infringed? The phrase "the exclusive right to the use of such trade mark" in section 39 carried, in his opinion, the implication of use of the mark for the purpose of indicating, in relation to the goods on or in connection with which the use took place, the origin of such goods in the user of the mark, by virtue of the matters indicated in the definition of trade mark contained in section 3 of the Act. If this construction were accepted, it was plain that the use of the word "Yeast-Vite" complained of did not infringe the right conferred by section 39, and that the appeal failed and should be dismissed with costs.

Lord Atkin and Lord Russell of Killowen concurred.

DISPENSING OF QUININE SULPHATE

ON December 1st, 1933, a firm of druggists was prosecuted at Birmingham for the inaccurate dispensing of medicine which, according to the prescription, should have consisted of 8 grains of quinine sulphate and 16 minims of dilute sulphuric acid in 8 oz. of chloroform water.

The certificate of the Public Analyst (Mr. H. H. Bagnall, B.Sc., F.I.C.) stated that the sample contained 9·5 grains of quinine sulphate (*i.e.* an excess of 19 per cent.) and 16·4 minims of dilute sulphuric acid. The proportion of quinine sulphate was calculated as the B.P. salt containing 11 per cent. of water.

Mr. C. E. Sage, F.I.C., who was called for the defence, stated that the quinine sulphate was in excess to the extent of only 3·6 per cent., and, in the course of his evidence, said that this statement referred to B.P. quinine sulphate containing 7·5 mols. of water, or 15·3 per cent. If the result were calculated to the salt containing 11 per cent. of water, it would appear that almost exactly 8 grains were present in 8 oz.

In view of the conflicting analyses, the Magistrates adjourned the case for the reserve portion to be submitted to the Government Chemist.

At the adjourned hearing, on January 12th, counsel for the defence argued that the Government Chemist's certificate was not admissible as evidence, there being nothing in the Food and Drugs Act to allow of this procedure. This objection was overruled, and the certificate was produced and found to confirm the result of the Public Analyst (0·210 grm., as compared with 0·209 grm., of anhydrous quinine per 100 ml.).

The defence contended that the residues obtained by the Public Analyst and by the Government Chemist were too high, owing to the fact that in each case ether had been used for extracting the quinine from the solution. According to Mr. Sage, such residue would contain water that was difficult to drive off at 100° C., and the apparent weight of quinine would thus be higher than was actually the case. In his opinion, his own analysis (0·175 grm. of anhydrous quinine per ml.) was correct, because he had used chloroform for the extraction, and, as this solvent did not take up water, moisture did not remain in the quinine as weighed.

The Magistrates decided that only a technical offence had been committed, and dismissed the case on payment of five guineas costs by the defendants.

MISBRANDING OF RADIUM OINTMENT*

THE product involved in this action was represented to be a radium preparation; the radium-content of the article, however, was found to be negligible, any therapeutic effects resulting from its use being dependent upon other drugs present.

On June 9th, 1932, the United States attorney for the Eastern District of Virginia brought an action, alleging that 11 jars of radium ointment had been shipped in inter-state commerce, from Denver, Colo., to Norfolk, Va., and charging misbranding in violation of the Food and Drugs Act.

Analysis of a sample of the article by the U.S. Department of Agriculture showed that it consisted essentially of potassium carbonate, small proportions of isopropyl alcohol, quinine and volatile substances (such as camphor, eucalyptol and menthol), soap, paraffin compounds, water and a radioactive substance. The radium-content was 13·4 $m\mu$ per grm.

It was alleged that the article was misbranded in that its name, "Radium Ointment," was misleading, since it contained drugs other than radium, upon which drugs the therapeutic effect of the article would be dependent and not upon radium, since the radium-content was negligible.

On November 10th, 1932, no claimant having appeared for the property, judgment of condemnation and forfeiture was entered, and it was ordered by the Court that the product be destroyed by the United States marshal.

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* U.S.A. Department of Agriculture: Food and Drug Administration. *Notices of Judgment under the Food and Drugs Act*, No. 20351. (Approved Dec. 1st, 1933.)

Department of Scientific and Industrial Research

THE STORAGE OF MEAT IN SMALL REFRIGERATORS*

THE aim of the Report is to supply knowledge of the causes of spoilage of meat and of the conditions by which they can be retarded in a refrigerator.

BACTERIAL SPOILAGE.—Samples of slimy meat from butchers in various parts of England have been submitted to bacteriological analysis. It was found that less than 0·1 per cent. have optima at 20° C., whilst the proportion having their optimum at 37° C. is relatively insignificant. In either instance only about a third of the bacteria are capable of growth at 4° C. and 0° C. The slime consists almost exclusively of organisms of the *Achromobacter* group, which have optimum temperature of growth at 20°–25° C., and grow well at 0°. Many strains are motile and liquefy gelatin. They do not induce putrefaction, and, so far as is known, are not pathogenic. Related species form the slime found on fish. A detailed study of some 100 strains of *Achromobacteria* isolated from meat has been published in the *J. Hyg., Cambridge* (1933, 33, 175).

SPOILAGE BY MOULDS.—The fungus most often found on meat is *Thamnidium chaetocladioides*. If the surface of the meat is slightly drier, and heavy contamination with mould has occurred, it may grow with exclusion of *Achromobacteria*. If moulds or bacteria grow directly on the fat, the taint effect is more marked.

THE EFFECT OF TEMPERATURE.—Joints hung at 11° ± 1° C. by day, and at 0·5° ± 0·5° C. by night, developed slime in 3 to 5 days. Similar joints hung for 2 to 4 days at 11° C. required only a further 4 to 6 days at 0° C. to become slimy. On the other hand, similar joints kept continuously at 0° C. did not become slimy until after the normal time of about 10 days. Smith and Tomkins (*Cold Stor. Prod. Rev.*, 1932, **35**, 56) found the storage-life of lean meat inoculated with spores of *Thamnidium* to be 8 to 10 days at 0° C.; if, however, the meat was inoculated with vegetable hyphae, stickiness might result after about 3 days.

RATE OF BACTERIAL GROWTH.—Sufficient multiplication of organisms on lean meat at 0° C. to form a visible and malodorous slime occurs when the bacterial count reaches about 30 million per sq. cm., which requires 8 to 11 days; at 4° C. this number may be reached in 4 or 5 days. The respective generation-times of *Achromobacter* (*i.e.* for one bacterium to divide into two) are 1·3 hours at 20° C., 6·6 hours at 4° C., and 9·1 hours at 0° C. during the most rapid period of growth.

RATE OF GROWTH OF MOULD.—The moulds commonly found on meat have, in general, an optimum temperature of about 20° C. Reducing the temperature to 0° C. would ensure a life-storage of meat exposed to infection by moulds some two-and-a-half to three times as long as at 5° C. Tables are given showing the effect of temperature on the growth of various moulds.

EFFECT OF DEGREE OF INFECTION.—Ordinary infection leads to spoilage in about 10 to 15 days at 0° C., and under exceptionally bad conditions meat may be spoiled in 3 or 4 days. The initial count of bacteria may range from 50 to 100,000 per sq. cm. Assuming the average generation-time of 12·1 hours for the bacterial population, the time taken for the critical value of 30 million organisms per sq. cm. to be reached, starting with initial loads of 10, 100, 1000, etc., can be worked out theoretically. It should be possible for meat to enter the store with not more than 100 to 1000 organisms per sq. cm. of surface, and it may then be stored for about a fortnight at 0° C.

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[*] Food Investigation, Special Report, No. 43. By R. B. Haines, Ph.D., and E. C. Smith, Ph.D. Pp. 26. London: H.M. Stationery Office, Kingsway, W.C.2. 1933. Price 9d. net.

EFFECT OF DRYING THE AIR.—Experiments are cited to show that variations in the drying power of the air in the store have no appreciable effect on the spoilage of lean meat.

SURFACES COVERED WITH CONNECTIVE TISSUE.—Connective tissue offers resistance to the diffusion of water, and meat with its natural coating of connective tissue can, therefore, be dried to an extent sufficient to prevent bacterial growth without too serious a loss of water from the underlying tissues.

CONTROL OF DRYING POWER OF AIR IN A STORE.—The drying power of the air in a store is best expressed in grms. lost in weight by a gel block of 20 per cent. gelatin per 100 sq. cm. surface per diem. So measured, the drying power of the air in several typical stores was found to lie between 0·5 and 2·5.

EFFECT OF INTERNAL HEAT ON DRYNESS OF AIR IN THE STORE.—The effect of the internal heat in a store is illustrated by the following table:

Heat supplied (cals. per hour)	Mean relative humidity Per cent.	Drying power (grms. per 100 sq. cm. per diem)
Nil	80	1·8
13,000	78	2·0
35,000	66	2·8
55,000	63	3·3
87,000	55	—

CHEMICAL INHIBITORS OF BACTERIAL GROWTH.—*Carbon dioxide.*—The growth of bacteria and moulds is retarded only so long as a sufficient concentration of carbon dioxide is maintained in the atmosphere. There is no evidence that the organisms are killed or permanently injured. The most satisfactory results are obtained with an atmosphere containing 10 to 20 per cent. of carbon dioxide. At 0° C. the growth of moulds is completely inhibited, and the rate of growth of the commonly occurring bacteria is reduced to less than one half. If concentrations higher than 20 per cent. are used, the meat is ultimately discoloured, the lean surfaces become brown and the fat pallid, owing to the conversion of oxyhaemoglobin into methaemoglobin.

Hydrogen cyanide.—According to Tomkins (*Proc. Roy. Soc.*, 1932, [B], **111**, **210**), 100 parts of hydrogen cyanide per million are required to inhibit the germination of the mould, *Trichoderma lignorum.* Monier-Williams (*Ministry of Health Report*, No. 60; ANALYST, **1931**, **56**, 47) recommends that a concentration of 20 parts per million should not be exceeded. Although cooking is said to remove most of the hydrogen cyanide, it is unlikely that this compound could safely be brought into practical use in the storage of meat.

Acetic Acid, Lactic Acid, Sodium Chloride.—The best of these is acetic acid, which can be most effectively used at a concentration of about 0·5 per cent. Meat heavily inoculated with a growing culture of *Thamnidium* was kept sweet for nine days by wiping it daily, from the fourth day onwards, with acetic acid of this concentration. On the sixth day, however, the colour of the meat began to deteriorate. Acetic acid in 2·5 per cent. concentration was only slightly more effective and turned the meat brown almost immediately. Acetic acid leaves a distinct, though not objectionable, taste. A 5 per cent. solution of lactic acid was only as effective as 0·5 per cent. acetic acid. The vapour of acetic acid does not deter the growth of moulds; although meat kept over solutions (1 : 10) of acetic acid took up the odour of the acid, there was no inhibition of mould-growth.

Treatment with a 1 per cent. solution of common salt was useful, the meat keeping for 8 days; this suggests that the mechanical removal of growing mould from the surface must play a considerable part in the success of the treatment.

Disinfectants.—Disinfectants are sometimes recommended to prevent spoilage. A commercial preparation of sodium hypochlorite, used at the recommended concentration, caused almost immediate browning of the surface. Most disinfectants lead to deterioration in the appearance and flavour of meat.

ULTRA-VIOLET LIGHT.—Bovie and Klein (*J. Gen. Physiol.*, 1918, **1**, 331) found that organisms sensitised by a sub-lethal dose of ultra-violet light are rapidly destroyed by moderate heat. Various lamps have been designed to apply these principles in commercial practice, but it is extremely difficult to ensure irradiation of the entire surface of even small joints; the spores of coloured moulds and certain bacteria are said to be very resistant to the radiation (Norton, *Newer Knowledge of Bacteria and Immunology*, University Chicago Press, 1928). Nor is it known to what extent radiation or its products (*e.g.* ozone, peroxides) may influence the colour or flavour of meat.

CHEMICAL AND ENZYMIC CHANGES IN STORED MEAT.—The browning (due to the formation of methaemoglobin) which lean meat undergoes in cold storage requires the presence of traces of oxygen, and, as it is impracticable to exclude oxygen from the store, there is no ready means, short of pickling, of preventing the discoloration. Drying the muscle may prevent browning (Brooks, *Biochem. J.*, 1929, **23**, 1391), but this in itself changes the colour of the meat. If the surface of the meat is free from bacterial growth, it should retain its bright red appearance for at least three weeks. Oxidative rancidity of the fat is hardly noticeable after 10 weeks at 0° C. Similarly, autolysis of the tissues is very slow; the amount of such change in sterile meat at 0° C. was determined by Hoagland, McBride and Powick (*U.S. Dept. Agric.*, Bull. No. 133, 1917).

CONDITIONING OF MEAT.—It has been shown in an earlier report (Food Investigation Special Report, No. 36) that the increase in the tenderness of meat on hanging is more pronounced in the coarser joints, and for this reason it is worth while hanging the whole quarter rather than a few choice cuts. With reasonable precautions it should be possible to hold beef for 17 days in a small refrigerator.

APPENDIX.—This contains typical examples of faults in the use of small refrigerators.

Fiji

ANNUAL REPORT OF THE GOVERNMENT CHEMIST FOR 1932

IN his Annual Report the Government Chemist (Mr. W. J. Blackie, M.Sc., A.I.C.) states that 686 samples were analysed in 1932, as compared with 717 in the previous year. The work done comprised routine services for the Medical, Customs, Agricultural and Public Works Departments.

MILK.—Of the 409 samples examined, 375 were received in connection with an investigation into the quality of Fiji milk from nine cows fed under normal conditions. Samples were collected daily during the first two months of the investigation, and then twice weekly until the 20th week. The average results for the whole period ranged from 3·8 to 4·8 for fat, and from 8·52 to 9·50 for solids-not-fat. The results show that Fiji milk can conform to the Pure Food Act, which requires milk to contain 3·2 per cent. of fat and 8·5 per cent. of solids-not-fat. Of the 33 samples submitted by the sanitary inspectors at Rewa and Suva, 15 failed to satisfy the legal requirements, but in many cases the poor quality of the milk was due to the Indian custom of removing the foremilk and permitting the calf to remove the strippings.

HOP BEERS.—Ten samples, submitted by the Police Department for determination of the alcoholic content, contained from 3·28 to 10·71 per cent. of proof spirit. Three other samples were not examined, since the regulation requiring the addition of a heaped teaspoonful of sodium salicylate, to prevent fermentation, had not been observed. Practically every sample examined contained excessive quantities of alcohol. Prosecutions were instituted in most cases, and substantial fines were imposed.

POISONING WITH NITROBENZENE.—Fifteen samples were submitted in connection with the deaths of two Fijians. The presence of prussic acid was suspected from the odour at the post-mortem examination, but chemical examination showed that nitrobenzene was present in each case, 20·5 and 6·1 grms., respectively, being isolated from the stomach-contents. Apparently, material that had been used in connection with explosives had been drunk in mistake for whisky.

KEROSENE IN CHARRED CLOTHING.—A bottle containing a fluid with blue fluorescence and a quantity of charred clothing were submitted by the police. The liquid proved to be kerosene, as supplied by the Shell Oil Company, and a similar liquid was extracted with petroleum spirit from the charred clothing.

BLOODSTAINS.—Twenty-seven articles were examined for bloodstains, including cane-knives (a favoured Indian weapon), clothes, mosquito nets, woodwork, mats, earth, etc. In practically every case the presence of mammalian blood was confirmed. After a sorting test with benzidine, glacial acetic acid and hydrogen peroxide, tests involving the separation of corpuscles, formation of haemin chloride and spectroscopic examination were applied. Bloodstains on rusted steel, etc. may be readily characterised up to a week or ten days by the haemin crystal test. Older stains fail to respond to the test in the presence of much iron oxide. It is also extremely difficult, and in many cases impossible, to obtain haemin crystals from bloodstained soil. However, spectroscopic examination is generally successful if blood is present in samples of this type.

PREPARATION OF ESTERS OF CHAULMOOGRA OIL.—A new process for the production of esters has been developed, in which the reacting materials are stirred rapidly and continuously at a temperature between 40° and 60° C. Observations have shown that at about 60° C. ester formation is rapid, provided the reactants are brought into intimate contact. By heating the materials on a controlled hot plate and stirring rapidly by means of an electric stirrer, a product of the same colour as that produced in the cold process was obtained in a much shorter time. It is necessary to fit a reflux water-cooled condenser to the reaction bottle and to observe the temperature from time to time by means of a thermometer immersed in the reacting materials. Esterification is complete in about 40 hours.

These products have not as yet been completely examined chemically. The values for the refractive index (n_D^{40}) for the esters prepared as above were:—(i) Cold process, 1·4550; (ii) hot process *plus* distillation, 1·4565; (iii) hot process without distillation, 1·4548; (iv) new process, 1·4555.

MUSTARD OIL AND EPIDEMIC DROPSY.—Fifteen samples of mustard oil were submitted by the Medical Officer of Health in connection with an outbreak of epidemic dropsy. A similar examination was made in 1926, when it was found that some of the samples were adulterated with sesame or linseed oil, but no toxic substances could be found. Several samples were also submitted to Professor Hilditch, who found that some of them were adulterated with sesame and others with poppy or linseed oil, but no pathogenic organisms were present. In his opinion, the oil could not in any way be connected with the outbreak of epidemic dropsy in Fiji. This opinion, however, appeared to be contrary to the findings of the Medical Department, as the result of some experiments carried out at Suva gaol.

In 1927 the matter was referred to the Government of India, who supplied full details of the position in India. Examination of the literature from India affords very little support for the adulterated mustard oil theory. Modern ideas incline to a deficiency theory or to the ingestion of a specific fungus growing on rice.

Six of the samples of mustard oil examined in 1932 gave abnormal analytical values, corresponding with the presence of approximately 40 per cent. of linseed oil. No toxic chemical substance of any kind could be found. If, from a medical standpoint, these mustard oils are regarded as responsible for the recent outbreak of epidemic dropsy, this can only be ascribed to the linseed oil. Although there is no information available as to the effect of linseed oil when ingested over a long period, it would appear improbable that this oil could cause the disease.

Federated Malay States

ANNUAL REPORT OF THE INSTITUTE FOR MEDICAL RESEARCH FOR 1932

THE chemical work required by various Government Departments is carried out in the Chemical Division of the Institute, the Chief Chemist being Mr. R. W. Blair, F.I.C. The total number of samples analysed during the year was 6302, as compared with 5208 in 1931. These included 2638 samples of water for routine analysis before and after chlorination, 1002 samples of milk, 466 for biochemical examination, and 1643 samples of coins and coining materials for the Police Department.

MILK.—The 1002 samples of fresh milk were taken by inspectors under the Sale of Food and Drugs Enactment from vendors in various towns and villages. The Enactment prescribes that milk must contain not less than 3·25 per cent. of fat, and not less than 8·25 per cent. of solids-not-fat. One hundred and twenty-four samples failed to comply with the standards. It cannot be too strongly emphasised that the adulteration of milk by the addition of water is particularly serious in a country where the water used for the purpose is probably taken from polluted sources.

CONDENSED MILK.—The minimum standards for sweetened condensed milk are 9 per cent. of fat and 31 per cent. of milk solids (including milk-fat), and for unsweetened condensed milk 8 per cent. of fat and 28 per cent. of milk solids. Ten of the 20 samples received failed to comply with the standards.

TOXICOLOGICAL EXAMINATIONS.—Poisons were identified in 101 of the 181 exhibits examined. Formic acid was found in 21 cases, arsenic in 14, datura in 11, and formalin in 5.

LEAD IN COSMETICS.—Thirteen of 20 samples of face powder examined were found to contain lead, usually in the form of carbonate. A rule has been gazetted under the Sale of Food and Drugs Enactment, 1913, which prohibits the sale, advertisement for sale, or importation into the Federated Malay States, of cosmetics containing lead or any compound thereof.

EVALUATION OF QUININE EXCRETION BY MEANS OF MAYER'S REAGENT.—Mayer's mercuric chloride reagent is commonly employed in the course of malarial treatment to detect the presence of quinine in urine. In the course of some 1300 recent examinations of urine Dr. J. W. Field has noted certain anomalies in connection with the test. In alkaline urine containing quinine there appears to be a critical concentration of the alkaloid, the level varying with the degree of alkalinity, below which there is no precipitation with Mayer's reagent. Above that concentration precipitation takes place, although to a less extent than in acid urine. The difficulty may be avoided by using Tanret's acid reagent (3 grms. of potassium iodide and 1 grm. of mercuric chloride in 20 ml. of glacial acetic acid, diluted with water to 60 ml.).

The statement that Mayer's reagent precipitates albumin is, generally speaking, incorrect. From acid urines it precipitates albumin, but not from neutral or alkaline urines. When quinine and albumin are both present the quinine alone is usually precipitated by the reagent, the amount of precipitate varying inversely with the concentration of the albumin. This uncertainty may be avoided by using Tanret's reagent, which invariably precipitates the albumin as well as the quinine.

Preliminary filtration of urine is seldom necessary. Urates dissolve readily on the addition of tap water, and a deposit of phosphates disappears on the addition of acetic acid. Cloudiness due to bacteria may be prevented by the addition of a few drops of formalin, which does not interfere with the reaction.

Tanret's acid solution is an excellent test reagent for albumin when alkaloids are not present; it is more sensitive than the heat test or the use of Haller's reagent, showing the presence of a trace of albumin in urine within a few seconds.

Standardisation of Biological Stains

In view of the importance of stains and staining materials used by microscopists engaged in biological investigation and research, and with a view to mitigating the variability of stains at present available, the Council of the Royal Microscopical Society has appointed a Committee to consider the standardisation of biological stains and staining materials manufactured in this country, and to make recommendations of standard specifications and tests for adoption, with a view to the certifying of manufactured stains conforming to such standards.

In addition to those Fellows of the Royal Microscopical Society appointed to serve on the Committee, the following official bodies have appointed representatives to serve thereon:—Medical Research Council, Royal Society of Tropical Medicine and Hygiene, Institute of Chemistry, the Chemical Society, Society of Chemical Industry, Pathological Society, and the Physiological Society.

The Committee has held several meetings, and the drafting of standard specifications for methylene blue, acid fuchsin, and eosin is under consideration. Other stains will be dealt with as soon as the biological tests of those in hand have proved them to be satisfactory. In addition, a standard specification for xylol for microscopical purposes is receiving attention.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs Analysis

Chemical and Spectrophotometric Detection of Gelatin in Soup-Cubes. H. Mohler, E. Helberg and F. Almasy. (*Z. Unters. Lebensm.*, 1933, **66**, 602–606.)—The examination of a sample of soup-cubes (*B*) containing a considerable amount of fat-free, crumbly matter insoluble in cold water and showing a much higher creatinine-content than a similar product of good quality (*A*), is described. The insoluble matter contained 17·5 per cent. of nitrogen and appeared to be gelatin; it was separated as follows:—Five grms. of the powdered cubes were boiled for 5 hours with 200 ml. of water and a little pumice in a 500-ml. Jena flask under a reflux condenser. After addition of 15 ml. of 10 per cent. tartaric acid solution, the boiling was continued for 30 minutes. The cooled liquid was almost neutralised (not made alkaline) with *N* sodium hydroxide solution, treated with

25 ml. of saturated zinc sulphate solution, and filtered. The precipitate contained proteoses, but, in presence of gelatin, this was present in the filtrate as glutose. The filtrate was shaken with 25 ml. of tannin solution (35 grms. of tannin, 500 ml. of water, and 15 ml. of glacial acetic acid) and filtered. The precipitate was washed with water, and the nitrogen in filter-paper and precipitate together was determined by the Kjeldahl method. A blank determination on a filter-paper and 1 grm. of tannin was also made. The proportion of the insoluble matter thus found in the cubes was 4·34–4·49 per cent. for *B*, and only 0·44 to 0·53 per cent. for *A*. The conclusion that this matter consisted of gelatin was confirmed by spectrophotometric examination of the coloured compound obtained by treating it with sodium hydroxide and picric acid. T. H. P.

Daily Variations in the Freezing-Point of Milk. H. A. Schuette and E. O. Huebner. (*Wisconsin Acad. Sci. Arts and Letters*, **1933, 28,** 267–274.)—The analyses were made by the methods of the A.O.A.C., and the Hortvet cryoscope was used for making the freezing-point determinations. The milk used was supplied by well-fed healthy individual cows in the herd of the College of Agriculture, University of Wisconsin. Their diet was a hay-silage-grain mixture, the grain consisting of maize (corn), oats, bran, and linseed meal. Five breeds were represented among the eight cows chosen for the investigation, and two series of observations on composite morning and evening samples were made. The following results were obtained with the milk of a Holstein cow at the end of her lactation period, and with the milk of a Jersey cow during the eleventh month of the lactation period:

	Holstein cow, No. 1				Jersey cow, No. 8			
	Max.	Min.	Aver.	Mean dev'n from aver.	Max.	Min.	Aver.	Mean dev'n from aver.
Fat, per cent.	6·00	3·45	4·70	±0·36	7·20	5·00	5·46	±0·32
Lactose ,,	5·13	3·71	4·81	0·23	5·66	4·64	6·08	0·10
Ash ,,	0·97	0·80	0·87	0·03	0·76	0·71	0·73	0·009
Protein (by diff.) per cent.	6·55	4·84	5·47	0·38	4·41	3·72	4·05	0·082
Total solids ,,	16·92	14·68	15·87	0·53	16·92	14·84	15·31	0·29
Chlorine in ash ,,	0·15	0·07	0·086	0·084	0·056	0·03	0·044	0·061
Sp.gr. at 15·6°/15·6°C.	1·0410	1·0376	1·0398	0·0013	1·0354	1·033	1·0342	0·004
Freezing-point, °C.	−0·54	−0·55	−0·55	0·003	−0·54	−0·56	−0·55	0·002

The freezing-point determinations of the milk secreted by the Holstein cow (No. 1) were continued during the time of the colostrum flow—in this instance arbitrarily designated as that produced three days after parturition—and then, the return to normal secretion having again set in, for one week longer. The following results were obtained:

Day	1	2	3	4	5	6	7	8	10	11
Time	P.M.	A.M. P.M.	A.M. P.M.	A.M. P.M.	A.M. P.M.	A.M. P.M.	A.M. P.M.	P.M.	Composite	Composite
Period	Colostrum*	Colostrum	Colostrum	Normal†	Normal	Normal	Normal	Normal		
Freezing-pt., °C.	−0·562	−0·569 −0·568	−0·562 −0·555	−0·561 −0·542	−0·539 −0·542	−0·538 −0·541	0·541 0·538	0·541	−0·538	−0·539

* Average depression of freezing-point, −0·563.
† ,, ,, ,, ,, −0·540.

The following table summarises the freezing-points of composite morning and evening herd milk and that of individual cows:

	Lactation period			Freezing-points			
	At times of test Months	Total months	Duration of analyses Days	Max. °C.	Min. °C.	Aver. °C.	Mean dev'n from aver., °C.
1. Holstein ..	19·5	20·5	33	−0·54	−0·56	−0·56	±0·003
2. Holstein ..	7·5	10·5	30	−0·54	−0·55	−0·54	0·003
3. Brown Swiss ..	8·5	13·5	32	−0·53	−0·54	−0·54	0·002
4. Brown Swiss ..	1·0	13·5	30	−0·53	−0·55	−0·54	0·002
5. Guernsey.. ..	5·0	15·0	31	−0·54	−0·55	−0·54	0·003
6. Ayrshire	9·5	15·5	32	−0·53	−0·54	−0·54	0·002
7. Ayrshire	6·5	9·0	31	−0·54	−0·55	−0·55	0·003
8. Jersey	9·5	12·0	34	−0·54	−0·56	−0·55	0·003
Average ..				−0·54	−0·55	−0·54	0·002
Herd			90	−0·53	−0·55	−0·54	0·002

The following conclusions have been drawn from the results of the investigation:—(1) The freezing-point of the milk secreted by an individual well-fed cow does not, under normal conditions, vary more in a thirty-day period than does that of the herd of which she is a member. (2) This physical constant is independent of the period of lactation, but is affected by the presence of colostrum in the milk. (3) The animal itself regulates the concentration of those substances with which an osmotic equilibrium is maintained within the body.

Choline Factor of Egg-yolk and the Phosphatid-Lecithin Number of Egg-Lecithin. F. E. Nottbohm and F. Mayer. (*Z. Unters. Lebensm.*, **1933**, **66**, 585–592.)—To determine choline in egg-yolk, the fatty acids are removed from 2 grms. of liquid or 1 grm. of dried yolk (ANALYST, **1933**, **58**, 43), and the filtrate from the animal charcoal is evaporated to 20 to 50 ml., which suffices for two determinations. One-half of the liquid is treated by Roman's method (*Biochem. Z.*, **1930**, **219**, 218), the choline ennea-iodide being precipitated in a stout-walled centrifuge tube (about 30 ml.) by addition of 5 ml. of concentrated iodine solution to the ice-cooled solution, which is stirred after the addition and then left for 15 minutes in ice-water. The tube is centrifuged, and the supernatant liquid poured quickly through the asbestos layer of a short Allihn tube. The crystalline precipitate is freed from iodine solution by washing with 10 ml. of ice-water in small portions. The ennea-iodide is dissolved in warm alcohol, and the solution is made up with water to about 500 ml. and titrated with 0·1 *N* thiosulphate solution: 1 ml. ≡ 1·335 mgrm. of choline. The calculation to lecithin is based on the molecular weight 805. Determinations in this way of the choline-contents of the fresh yolks of hens' and ducks' eggs give results differing very little from 1 per cent.

For obtaining the lecithin from egg-yolk, the following modification of Brodrick and Pittard's procedure for milk (*Biochem. Z.*, **1914**, **67**, 382) is recommended:—About 3 grms. of the liquid yolk are stirred with 100 ml. of water and the mixture is shaken for 4 hours with 200 ml. of a 3 : 1-mixture of alcohol and ether. The filtered liquid is evaporated in a flat dish at about 36° C., and the residue is ground with 2 to 3 times its quantity of freshly-ignited and finely-ground sodium sulphate and extracted for 3 to 4 hours with chloroform. The residue from the chloroform extract is then used for the determination of choline, as described above. With hens' eggs it is found that practically the whole of the choline of the yolk is present in the form of choline-lecithin. With ducks' eggs, however, the lecithin separated shows appreciably less choline than the original yolk, and the yolk exhibits a non-emulsifiable constituent when mixed with water.

The ratio between total phosphatid and choline-lecithin, termed the phosphatid-lecithin or P : L number, furnishes a useful indication of the structure of these phosphatids, which consist mainly of choline-lecithin and cephalin. For the lecithins of hens' and ducks' eggs, this number is about 1·4 and 1·5, respectively. Calculated on the dry yolks, the total phosphatid, choline-lecithin and cephalin are, respectively, 19·99, 14·27, and 5·72 per cent. for hens' eggs, and 16·48, 10·90, and 5·58 for ducks' eggs. Liquid hens' and ducks' egg-yolks contain 8·53 to 10·90 per cent. and 7·96 to 9·77 per cent., respectively, of phosphatids.

T. H. P.

Determination of the Rancidity of Fats by Stamm's Reaction. S. Korpáczy. (*Z. Unters. Lebensm.*, 1934, **67**, 75–79.)—Stamm's use of *s*-diphenylcarbazide in vaseline oil as a reagent for detecting the alteration of fats (ANALYST, 1926, **51**, 416) cannot be used for comparative tests, as the reagent is used in suspension. This disadvantage is overcome by dissolving the reagent (0·5 grm.) in *s*-tetrachloroethane (100 ml.) by heating to boiling in a flask over a naked flame, cooling and filtering. As comparison liquids, use is made of aqueous solutions containing 0·5, 1, 1·5, 2, 3, 4, 5, 7·5, 10, 25, 50, 75, 100, 150, 200, 250, and 300 mgrms., respectively, of Bordeaux S per 100 ml. In addition, each of the first 9 of these solutions contains tartrazin to the extent of 50 per cent. of the Bordeaux S present, this percentage being dropped to 10 for the solutions containing 25 mgrms. and upwards of Bordeaux S per 100 ml.; such addition compensates for the yellow colour of the fat solution. Experiment shows that the reagent gives only slight colorations with aldehydes, organic peroxides, or pure fatty acids, and that the intense colorations formed with rancid fats are due to aliphatic hydroxy-acids, which may be produced from oleic and other unsaturated acids by the action of light, air and moisture. The reaction with the diphenylcarbazide is similar in some ways to Kreis's reaction, and is useful in supplementing this, although it does not follow a parallel course in all cases.

To make the test, *x* grms. of the melted fat, filtered, if necessary, are heated for exactly 3 minutes with *x* ml. of the reagent in a test-tube in a boiling water-bath, the tube being then rapidly cooled under the tap and dried, and the colour comparison made. The result is expressed as the number of mgrms. of Bordeaux S per 100 ml. in the matching solution. Fats giving values up to 0·5 are most probably fresh and unspoilt. Values between 1 and 2 indicate that the fats should be used quickly as they will not withstand prolonged storage. Values between 2 and 4 point to incipient rancidity, but, if there are no other contra-indications, such fats will pass as second-quality products. All fats showing values of 5 or more in the test must be regarded as inedible. T. H. P.

Isolation and Identification of some Hitherto Unrecorded Fatty Acids in Butter-Fat. A. W. Bosworth and J. B. Brown. (*J. Biol. Chem.*, 1933, **103**, 115–134.)—The methyl esters of the fatty acids of a typical specimen of creamery butter have been efficiently fractionated into thirty-seven fractions, and these fractions subjected to exhaustive examination. From a study of the curves derived from the iodine values of the fractions the presence of decenoic acid was predicted in the C_{10} fraction, and the presence of a hitherto unreported acid, tetradecenoic acid, in the C_{14} fraction. The presence of decenoic ($C_{10}H_{18}O_2$) and tetradecenoic ($C_{14}H_{26}O_2$) acids has been proved. The evidence for the occurrence of hexadecenoic (palmitoleic) acid and eicosenoic (gadoleic) acid was doubtful. By mere fractionation a high-boiling fraction with an iodine value of 99 was obtained, this demonstrating the presence of acids more unsaturated than oleic. This was further substantiated by the isolation of ether-insoluble polybromides from several of the higher fractions. All attempts to verify the occurrence of ordinary linolic acid, reported in butter-fat by Hilditch and Jones (ANALYST, 1929, **54**, 75) and by Eckstein (*J. Biol. Chem.*, 1932, **97**, 35), failed. There seems to be evidence of the occurrence of a C_{20}, a C_{22}, or a C_{24} acid with two double bonds. Highly unsaturated acids of the arachidonic type were found; these probably belong to the C_{22} series. From the four highest fractions there was isolated a mixture of saturated acids of high molecular weight, consisting principally of tetracosanoic (lignoceric) acid, with, probably, small amounts of behenic and cerotic acids. In view of these results, butter-fat appears to be the most complex of all known fats. P. H. P.

Linolic and Linolenic Acid Contents of Butter-Fat. H. C. Ekstein. (*J. Biol. Chem.*, 1933, **103**, 135–140.)—Holland, Garvey, Pierce, Messer, Archibald, and Dunbar (ANALYST, 1923, **48**, 555) questioned the presence, in butter-fat, of fatty acids more highly unsaturated than oleic acid. In marked contrast with that report, Hilditch and Jones (ANALYST, 1929, **54**, 75) and Hilditch and Sleightholme (ANALYST, 1930, **55**, 702) have reported that butter-fat may contain as much as 4·5 per cent. of linolic acid. In both instances the linolic acid content was calculated from the iodine values of the various fractions obtained by the distillation of the methyl esters. Owing to the discrepancy between these two reports, it seemed desirable to re-investigate the matter by a different method of procedure. The linolic and linolenic acid contents of samples of butter-fat, representative of the product produced in the State of Michigan, have, therefore, been calculated from the weights of crystalline bromide fractions. By this means it was calculated that the linolic acid content of the butter-fats analysed ranged from 0·17 to 0·25 per cent. The linolenic acid content varied from 0·07 to 0·17 per cent. The values shown for these unsaturated acids are probably too low, since a study of the methods used for their determination showed that, when they were added to butter, poor recoveries were obtained. However, even if one assumes, in the light of the recovery experiments, that the values obtained indicate only 50 per cent. of the linolic acid actually present in the fats examined, the figures obtained by making such a correction would by no means approach those given by Hilditch *et al.* It was demonstrated that the linolenic acid content of butter-fat could be increased by including linseed meal in the ration of cows.

P. H. P.

Fatty Oil from the Seeds of *Cassia Occidentalis* Linn. ("Wild Coffee"). A. Steger and J. Van Loon. (*Rec. Trav. Chim. Pays-Bas*, 1934, **53**, 28–30.)—These seeds were obtained from the island of St. Martin in the Lesser Antilles where, although they contain no caffeine, they are used as a substitute for coffee (under the names "negro," "wild" or "mogdad" coffee), concentrated extracts being also considered a cure for asthma. They are 4 to 5 mm. long, weigh about 20 mgrms., and consist of 75 per cent. of hard brown shell and 25 per cent. of an orange-coloured kernel. A yield of 2·3 per cent. of oil (9·3 per cent. on the kernels) was obtained by grinding them in a roller-mill, extracting the meal with petroleum spirit, drying the extract over sodium sulphate, decolorising with activated charcoal, filtering and evaporating under reduced pressure. The properties were as follows:—Saponification value, 178·7; acid value, 10·2; Reichert–Meissl value, 0·5; Wijs iodine value, 113·9; thiocyanogen value, 78·2; n_D^{15}, 1·4770; unsaponifiable matter (solid at room-temperature), 7·35 per cent.; total fatty acids soluble in petroleum spirit, 88·1 per cent. (Wijs iodine value, 115·8; thiocyanogen value, 76·8; m.pt. approx. 32° C.; acid value, 197·7; mean molecular equivalent, 284; n_D^{70}, 1·4462); saturated fatty acids (Bertram), 22·4 per cent. (saponification value, 202; mean-molecular equivalent, 278; m.pt., 51 to 54° C.; n_D^{70}, 1·4338). The fatty acids were brominated, and the bromine contents of the portions insoluble and soluble in ether were determined. The insoluble bromide melted at 185° C., and contained 63·3 per cent. of bromine. The acid isolated from it corresponded with 9, 12, 15-linolenic acid. The bromides soluble in ether were treated with cold petroleum spirit, and the insoluble portion was recrystallised from acetone. It melted at 115° to 116° C., contained 54·0 per cent. of bromine (which was a little higher than the theoretical 53·3 per cent., owing to the presence of a minute quantity of linolenic hexabromide, which is slightly soluble in ether but insoluble in cold petroleum spirit). This corresponded with 9, 12-linolic acid. The bromides soluble in cold petroleum spirit were de-brominated and oxidised with dilute alkaline permanganate solution. They yielded a dihydroxystearic acid. (m.pt. 130° to 131° C.), corresponding with 9-oleic acid; the mixed melting-point method was used as a final check on these methods of identification. The following values were then calculated by the method of Kaufmann and Keller (ANALYST, 1929, **54**, 304):—Glycerol residue (from the ester value) as C_3H_2, 3·8; saturated acids, 19·7; 9-oleic acid, 30·7; linolic acid, 31·4; linolenic acid, 6·3; unsaponifiable matter, 7·4; and volatile matter, 0·7 per cent. J. G.

Fatty Oil from Quince Seeds. A. Steger and J. Van Loon. (*Rec. Trav. Chim. Pays-Bas*, 1934, **53**, 24–27.)—Kernels of the quince (*Cydonia vulgaris*), after being crushed in a roller-mill and extracted with ether, yielded 19·2 per cent. (on the air-dry kernels) of a light yellow, almost odourless oil having a watery consistence at room-temperature, and giving the following analytical values:—Sp.gr. (15° C./4° C.), 0·9220; acid value, 15·3; saponification value, 194·2; ester value, 178·9; Wijs iodine value, 121·6; thiocyanogen value, 82·7; acetyl value, 14·7; n_D^{20}, 1·4738; saponification values of total fatty acids, 179·9 (neutral ethyl esters) and 191·2 (acetylated esters). The following results, obtained by the methods described in the preceding abstract, are given as percentages:—Unsaponifiable matter, 0·36; glycerol residue (as C_3H_2), 4·0; total fatty acids, 94·2 (a very soft butter-like mass, liquid at 25° C., and having an acid value of 197·5; Wijs iodine value, 127·4; n_D^{20}, 1·4474; thiocyanogen value, 85·7); saturated acids, 8·6; oleic acid, 42·5; linolic acid, 39·2; linolenic acid, 3·9; and volatile matter, 1·44 per cent. This analysis does not allow for hydroxy acids or oxidised acids, which, if they occur at all, are present only in small quantities, and are then probably oxidation-products. According to Herrmann (*Arch. Pharm.*, 1899, **237**, 358), quince-seed oil contains an unsaturated hydroxy acid, $C_{17}H_{32}(OH)$ COOH ("quince-oleic acid," "*Quittenölsäure*"). Its absence was proved by the fact that, if present, it would have had a pronounced influence on the isolation of 9-elaidic acid, whereas that acid was obtained without difficulty on applying the elaidin test to the unsaturated fatty acids separated by Bertram's method.

J. G.

Millet Seed Oil. A. Steger and J. Van Loon. (*Rec. Trav. Chim. Pays-Bas*, 1934, **53**, 41–44.)—The oil was extracted with ether from the ground whole seeds of millet (*Panicum miliaceum*), since it was suspected that oil from polished seeds undergoes oxidation and loss of lower fatty acids. The extract was dried, treated with activated charcoal, filtered and evaporated, and a yield of 3 per cent. was obtained of a pale yellow oil which had a characteristic odour and crystallised in the cold in laminae, consisting (according to Kassner, *Arch. Pharm.*, 1887, **66**, 395, 1081) of "panicol," $C_{12}H_{17}OCH_3$. The analytical values of the oil were as follows:—Sp.gr. (15° C. / 4° C.), 0·9383; acid value, 12·8; saponification value, 191·5; n_D^{70}, 1·4577; Wijs iodine value, 129·0; thiocyanogen value, 80·0; acetyl value, 16·9; Reichert–Meissl value, 1·76; unsaponifiable matter (not completely fused at 100° C., owing probably to the presence of panicol, m.pt., 270° C.), 3·3 per cent.; total fatty acids, 88·7; glycerol residue (as C_3H_2), 4·0; volatile matter, 4·0 per cent.; there are also probably other volatile constituents which are lost during the analytical procedure. The fatty acids soluble in ether formed a mass of butter-like consistence, which was fluid at 25° C., but the isolation involved some difficulty, owing to the separation of albuminous and mucilaginous matter; and, although there was evidence (from the acetyl value) of the presence of a small quantity of hydroxy acids, it was not possible to purify the acids further, even by distillation under reduced pressure, on account of the above-mentioned foreign matter. The following composition was deduced from the results obtained by bromination (*cf.* preceding abstract), ozonisation, and a separation by Twitchell's method, and was calculated by the method of Kaufmann and Keller (ANALYST, 1929, **54**, 304):—Wijs iodine value, 142·2; thiocyanogen value, 86·6; n_D^{70}, 1·4493; acid value, 196·0; mean molecular equivalent, 287; saturated acids, 10·7; saponification value of the ethyl esters, 183·5 (and of the acetylated esters, 194·5); oleic acid, 23·9; linolic acid, 46·9; linolenic acid, 7·2. These figures do not include hydroxy or oxidised acids which, it is considered, are probably produced during the drying process, and no evidence of the existence of Kassner's *Hirseölsäure* was obtained. (*Cf.* Smith and Waller, ANALYST, 1933, **58**, 319.)

J. G.

Rye Oil. II. Properties as affected by Choice of Solvent. A. W. Stout, H. A. Schuette and R. G. Fischer. (*J. Amer. Chem. Soc.*, **1934**, **56**, 210–211.)—An investigation has been made of the relation of 8 solvents to the properties of rye oil, and it is shown that the amount of oil recoverable from the embryo is a function of the solvent, as are also the degree of pigmentation of the oil, its physical and chemical properties, and the proportion of unsaponifiable matter and phosphorus present. The colour of a 1 per cent. solution of the oil in petroleum spirit was measured in a Rosenheim-Schuster colorimeter, and expressed in Lovibond units. The unsaponifiable matter was determined by the method of the Sub-Committee on Determination of Unsaponifiable Matter in Oils and Fats of the Society of Public Analysts (ANALYST, 1933, **58**, 203).

Solvent.	Oil per cent.	Colour in 1 per cent. solution. Yellow	Red	Sp.gr. 25/25°C.	$n_D^{20°C}$	Iodine value (Wijs)	Unsaponifiable matter Per cent.	Lecithin (P×26) Per cent.
Petroleum spirit ..	11·46	3·5	0·5	0·9220	1·4750	138·42	9·34	1·03
Ethyl ether	13·66	3·2	0·5	0·9297	1·4732	135·05	8·95	1·78
Carbon tetrachloride	13·84	2·1	0·8	0·9341	1·4773	137·44	8·25	3·18
Ethylene dichloride	14·13	4·9	0·6	0·9329	1·4781	139·03	8·86	3·75
Carbon disulphide ..	14·14	6·1	0·4	0·9296	1·4780	139·50	10·00	2·97
Benzene	14·45	4·4	0·5	0·9308	1·4789	133·80	9·08	4·11
Chloroform	15·57	3·5	0·6	0·9483	1·4772	133·90	8·09	7·26
Acetone	17·23	3·7	0·7	0·9286	1·4753	136·85	9·01	1·67

(*Cf.* Croxford, ANALYST, 1930, **55**, 735.) D. G. H.

Wisconsin-grown Tobacco Seed Oil. W. L. Roberts and H. A. Schuette. (*J. Amer. Chem. Soc.*, 1934, **56**, 207–209.)—Tobacco seed oils from different localities of Wisconsin had the following characteristics:—Sp.gr. 20°/20° C., 0·925–0·9260; $n_D^{20°}$ C., 1·4755–1·4763; solidifying pt., −14° to 16° C.; "titre" test, 18·1°–18·2° C., saponification value, 189·1–190·7; iodine value (Wijs), 142·7–146·7; Hehner number, 95·4 to 95·9; Reichert–Meissl value, 0·26 to 0·28; Polenske value, 0·11 to 0·13; unsaponifiable matter, 1·24 to 1·25. The composition of 2 samples of seed (*a*) strain unknown, (*b*) Havana, in percentages were: Moisture, 4·36, 3·61; ether extract, 38·90, 38·54; crude protein, 18·92, 19·02; ash, 3·66, 3·83, consisting of soluble ash, 1·45, 1·47 (of alkalinity, 9·4, 9·3 ml. 0·1 *N* acid per grm.); insoluble ash, 2·21, 2·35 (of alkalinity 25·2, 28·4); nitrogen-free extract, 9·97, 10·18. The average percentage compositions of the oils was: Palmitic acid, 3·1; stearic, 4·8; oleic, 16·2 and linolic acid 70·4, with unsaponifiable matter 1·25. Those highly unsaturated usually associated with drying oils were absent, and the predominating linolic acid appears to be present in two isomeric forms.

D. G. H.

Constituents of the Petroleum Spirit Extract of the Blossoms of Yarrow. R. L. McMurray. (*Amer. J. Pharm.*, 1933, **105**, 573.)—The air-dried flowers of *Achillea millefolium*, Linn., yielded, on extraction with petroleum spirit, 1·86 per cent. of a crude, dark green, wax-like fixed oil having an average saponification value of 111·5, iodine value 56·6, acid value 36·9, and of unsaponifiable matter 22·75 per cent. The fatty acids, which included *iso*-valeric acid and other lower members of the series, amounted to 52·5 per cent. of the original fatty material. The unsaturated fatty acids contained linolic and oleic acids, and the saturated fatty acids consisted mainly of myristic, palmitic, an undetermined acid and cerotic acid. Ceryl alcohol was found in the unsaponifiable matter; also a sterol and the saturated hydrocarbon triacontane (m.pt. 65·6° C.). D. G. H.

Determination of Chlorogenic Acid in Roasted Coffee. C. Massatsch. (*Z. Unters. Lebensm.*, 1934, **67**, 88–90.)—According to Plücker and Keilholz (ANALYST, **1933**, **58**, 701), treatment of coffee beans with steam under pressure results in marked diminution of the content of chlorogenic acid. Coffee treated in this way is a commercial product (sold as "Idee" coffee), and three samples were found to contain, respectively, 4·27, 4·38, and 4·30 (or 4·50, 4·44, and 4·57) per cent. of chlorogenic acid, as determined by the Hoepfner procedure (ANALYST, **1933**, **58**, 100, 702; *cf.* also Griebel, ANALYST, **1933**, **58**, 621) with the absolute colorimeter (or the Pulfrich photometer). For comparison with these, large samples of Menado, Guatemala, Rio and Santos raw coffees were roasted (without steam-pressure treatment) to the same colour as the "Idee" coffees, and determinations of the chlorogenic acid were made as before. The percentages obtained with the two instruments were, in order: 3·48 (3·32), 4·00 (4·30), 4·80 (4·72), and 4·27 (4·52). Hence, any loss of chlorogenic acid produced by steam-pressure treatment of the coffee cannot serve as the basis of a proof that such treatment has been employed in any particular case. T. H. P.

Determination of Capsanthin in Ground Paprika Products. L. Benedek. (*Z. Unters. Lebensm.*, 1933, **66**, 600–602.)—The red colouring matter, capsanthin, $C_{34}H_{48}O_3$, on which the colouring properties of Hungarian paprika depend, may be determined in ground paprika preparations by the following modification of Zechmeister and Cholnoky's method (*Annalen*, 1927, **455**, 79):—A corked tube, containing 2 grms. of the air-dry product and 50 ml. of a 1 : 1-mixture of ether and petroleum spirit, is mechanically shaken for 30 minutes, and then centrifuged for 10 minutes in a milk centrifuge. Five ml. of the resulting clear liquid are made up to 100 ml. with the mixture of ether and petroleum spirit, the colour of this solution being compared with that of a 100-mm. column of 0·2 per cent. potassium dichromate solution. The depth of the matching column of the paprika extract is divided into 125 to obtain the number of grms. of capsanthin in 1 kilo. of the preparation. The results (10) obtained varied from 3·55 (3·31 to 3·95) for paprika meals of the highest quality to 1·73 (1·39 to 2·05) for third-quality products. One-seventh of the amount of capsanthin represents the carotene present. T. H. P.

Biochemical

Iodine Survey of New Zealand Live Stock. E. Mason. (*Trans. N. Zealand Institute*, **1933**, **63**, 373–388.)—The determination of the iodine-content of thyroid glands from a large number of sheep and lambs from Otago and Southland, New Zealand, has shown that, although the relative effects of age, sex, and moisture on the percentage of iodine have been studied, data are not yet sufficient for the application of statistical methods. Between the weight of the gland and its percentage content of iodine there is an inverse relationship, which, however, is almost negligible until the percentage of iodine has fallen below the critical value of 0·03 per cent. of fresh thyroid weight. Below this value the weight of gland increases fairly rapidly, with a decrease in the percentage of iodine. Spontaneous enlargement of the thyroid may then occur, and is usually present in individual cases in flocks where the average percentage of iodine in the glands is below 0·03 per cent., but whole flocks are occasionally affected. The enlargement has not been noted in any district where the average percentage of iodine is above the critical value. In the case of an outbreak of congenital goître among lambs, cures were usually effected, by treatment with tincture of iodine, if the lambs survived three days. With light sandy soils, and more or less heavy rainfall, leaching of soluble salts may occur, resulting in diminution of iodine. Iodine-feeding appears to have little effect on the iodine-content of the thyroid glands of sheep, so that, since the total iodine in the gland can be increased by giving iodides, either the "lick" containing 3 oz. of iodide per cwt. was not eaten in sufficient quantity, or iodide had been lost by leaching or by decomposition accompanied by volatilisation of free iodine. Incorporation of iodide in the "lick" is, however, advised for certain districts, and experiments with such iodised "licks" are being carried out. D. G. H.

Nutritive Deficiencies of Gelatin. H. D. Kruse, H. G. Day and E. V. McCollum. (*Amer. J. Hyg.*, 1934, 19, 260–269.)—Feeding experiments on 16 rats for 104 days showed that gelatin could supply protein nourishment if it was supplemented with tryptophan, tyrosine, cystine, histidine and a mono-amino acid constituent of casein. The last-named is the insoluble portion of the butyl-alcohol extract of casein. All rats, even those with satisfactory growth records, however, showed renal lesions at the autopsy. R. F. I.

Determination of Glycogen. M. Sahyun. (*J. Biol. Chem.*, 1933, **103**, 203–208.)—In an earlier paper by Sahyun (ANALYST, 1932, **57**, 51) on the determination of glycogen in tissues, several improvements were introduced into the well-known method of Pflüger, one of which was the addition of small quantities of activated charcoal to insure the complete precipitation of glycogen. In testing Sahyun's method, Good, Kramer and Somogyi (*J. Biol. Chem.*, 1933, **100**, 485) used 400 mgrms. of charcoal instead of 50 mgrms., and substituted norit for Merck's charcoal, and reported that incomplete hydrolysis of the glycogen adsorbed on charcoal takes place. Since its publication Sahyun's method has been used in more than 1000 determinations in the author's laboratories, with excellent results. However, in view of the criticism on the use of charcoal, further evidence is now furnished on the recovery of glycogen as glucose from the charcoal, and special stress is laid upon the amount that can be safely used in glycogen determinations. The evidence presented clearly indicates that the addition of small amounts of charcoal to insure the complete precipitation of glycogen does not interfere in the least with its hydrolysis. However, it is emphatically stated that the charcoal, whether norit or Merck's, should not be added in quantities of more than 50 mgrms. A small quantity of 20 to 30 mgrms. is easily estimated on the tip of a spatula without weighing, and is sufficient to accomplish the purpose for which it is added. When larger amounts of charcoal are used, the data presented in this investigation are in harmony with those obtained by Bancroft and Fry (*J. Biol. Chem.*, 1933, **100**, 255), and by Good, Kramer and Somogyi. A great saving of time may be effected by hydrolysing the precipitated glycogen in 5 *N* sulphuric acid. The author considers 20 minutes to be the optimum time, although 15 minutes were observed to be sufficient. The final volume of the 5 *N* acid solution should be kept as small as possible. P. H. P.

Iron-Content of the Whole Blood of Normal Individuals. O. M. Helmer and C. P. Emerson, Jr. (*J. Biol. Chem.*, 1934, **104**, 157–161.)—In the course of an investigation of the iron-content of the whole blood of normal individuals, iron values, haemoglobin values and oxygen capacity-values were obtained which differed from those generally reported normal in the literature. Since the oxygen-capacity method is the standard method for the determination of the haemoglobin-content of blood, simultaneous determinations of oxygen-capacity by the method of Van Slyke and Neill (*J. Biol. Chem.*, 1924, **61**, 523) and of iron by the method of Kennedy (ANALYST, 1927, **52**, 603) were made on the blood of a series of normal men and women. The data obtained show that there is a close agreement between the haemoglobin-contents of normal human blood, as determined by its iron-content, and oxygen-capacity. Therefore, the determination of iron offers an easy means for the determination of the haemoglobin-content of blood or for the standardisation of colorimetric methods for the determination of haemoglobin. The blood iron-content of eighteen normal men, determined by the Kennedy method, varied from 49·3 to 57·2 mgrms. per 100 ml., with an average of 52·5 mgrms. The blood iron-content of ten normal women varied from 42·0 to 49·8 mgrms. per 100 ml., with an average of 45·8 mgrms. In order to determine whether the earlier discrepancies in the iron values might be explained by the methods used for the determinations of the iron-content, a comparison was made between the Kennedy method and that of Wong (*J. Biol. Chem.*, 1928, **77**, 409). Higher iron values were obtained with the Kennedy method than with the Wong method. Although the simplicity of the Wong method recommends its use, in the experience of the authors the Kennedy method has proved to be more satisfactory. P. H. P.

Method for the Quantitative Determination of Indoxyl Compounds in Blood. H. Sharlit. (*J. Biol. Chem.*, 1934, **104**, 115–120.)—A method for the quantitative determination of indoxyl compounds in blood is described in detail. The procedure differs essentially in but one respect from that recently presented by Sharlit (*J. Biol. Chem.*, 1932–33, **99**, 537) for the determination of indoxyl compounds in urine. For bloods containing any but exceedingly high concentrations of indoxyl, all reactions must be carried out at room temperature. The use of a boiling water-bath, as indicated for the determination in urine, gives small but definite increments in colour formation, owing to the presence of substances other than indoxyl. Whereas solutions of indican give identical values with both the urine and blood methods at the temperature of boiling water, neither method is quantitative with amounts of indican in excess of 0·015 mgrm. when carried out at room temperature. Therefore, to obtain quantitative results, either room-temperature or boiling-water temperature must be used in the procedure, as dictated by the absolute amount of indican in the blood sample tested. The results show that normal blood contains less than 0·06 mgrm. of indican per 100 ml. The determination is carried out on 2 ml. of blood plasma. Haas (*Münch. med. Woch.*, 1915, **31**, 1043), who adapted the method of Jolles (*Arch. Pharm.*, 1928, **266**, 40) to blood, used 40 ml. of serum to determine normal concentrations. This he found to be between 0·02 and 0·08 mgrm. per 100 ml. in conformity with the findings of the author. It is shown that, with nitrogen retention, the concentration of indican in the blood may rise to more than 100 times the maximum in normal blood. P. H. P.

Human Milk Studies. XIV. Critique of the Determinations of Nitrogenous Constituents. B. N. Erickson, N. Stoner and I. G. Macy. (*J. Biol. Chem.*, 1933, **103**, 235–248.)—The methods for the preparation of protein-free filtrates of human milk, with particular reference to the adaptability of the sodium tungstate and sulphuric acid precipitation procedure, have been studied. A modified method is presented which involves the use of 0·1 ml. of 10 per cent. sodium tungstate solution and 0·2 ml. of 0·666 *N* sulphuric acid per 1 ml. of human milk for complete precipitation of proteins and preparation of filtrates adaptable to the standard procedures of blood analysis and gasometric determinations for non-protein nitrogen constituents. With the above amounts of tungstate and acid a p_H range of 2·5 to 2·8 was secured, at which precipitation of protein seemed to be at a maximum and the filtrates practically free from excess tungstic acid. It is of interest to note, in connection with the requirement for human milk of only one-tenth the amount of sodium tungstate used for the precipitation of blood proteins, that human milk contains about one-tenth the protein of blood. A comparative study of tungstic acid and trichloroacetic acid as protein precipitants demonstrated the presence of polypeptides in fresh human milk. The gradual increase of polypeptide nitrogen in the milk after its removal from the breasts demonstrated the occurrence of proteolysis. The increase of amino acid nitrogen after the hydrolysis of the protein-free filtrates with hydrochloric acid showed the presence of simple peptides or conjugated amino acids in fresh human milk. The existence of a proteolytic enzyme and an enzyme capable of converting urea into ammonia has also been demonstrated in human milk. The differences obtained in methods of precipitation present opportunities for a more comprehensive study of the nitrogen constituents of human milk which have been little investigated heretofore, and which promise to be of definite significance in the physiology and abnormalities of milk secretion. P. H. P.

Silicosis. W. R. Jones. (*Inst. Min. and Metall., Bull.* No. 352, Jan. 1934, 1–42.) —After summarising his previous work on the causation of silicosis (*cf.* ANALYST, 1934, **124**) the author supports and illustrates his conclusions by new observations. At the International Congress on silicosis, held at Johannesburg in August, 1930, the definition finally accepted was that silicosis is a "pathological condition of the lungs due to the inhalation of silicon dioxide," and to produce this condition "silica must react in the lungs in a chemically uncombined state." It is submitted that uncombined silica is not the chief cause of silicosis in the cases examined. This is proved by mineralogical and chemical evidence from the lung residues, by examination under the petrological microscope of sections of silicotic lungs, and by the following facts, *inter alia*: (*a*) The rocks in the South Wales coalfield give rise to dust that produces silicosis, whereas the quartz in the sandstones in the Scottish coalfields has not produced any authenticated cases of silicosis. (*b*) The gold-bearing quartz conglomerate of South Africa gives rise to dust that has produced thousands of cases; the gold-bearing quartz rock of the Kolar goldfield, India, contains more quartz than the South African rock, and yet no case of the disease has been produced by its dust. These differences are explained when microscopic sections of the respective rocks are examined with the petrological microscope under crossed nicols. Those rocks known to have produced silicosis show acicular aggregates of sericite in the matrix between the quartz pebbles, whereas there is complete absence of sericitisation in the rock whose dust has not given rise to silicosis. For the same reason rocks which do not come under the category of "silica rocks," as defined in the Silicosis Scheme under the English law, have been the cause of silicosis in some of the anthracite collieries in South Wales. Observation has shown that the finer the dust in the underground Witwatersrand gold mines in South Africa, the greater is the ratio of sericite fibres to quartz particles. This is true of any rock containing quartz and sericite.

The method of examining konimeter dust spots by opaque illumination, as practised until recently in South Africa, gives untrustworthy and misleading results. What appears in reflected light as one particle too large to be counted, is resolved, when examined by transmitted polarised light, into an aggregate of particles. Moreover, the preliminary treatment of the dust-spot with dilute (1 : 1) hydrochloric acid carries away in suspension many fibres of sericite.

The suggestion, made in 1928, that "powdered shale" should be spread in mines to prevent silicosis was based on the supposed absence of silicosis in British collieries. Since that date, however, scores of cases have been contracted in the anthracite collieries in South Wales; these collieries are among the driest and dustiest in this country, and much of the dust is from shale. Other preventive measures, such as wet drilling and water-spraying, have not proved effective, and it is suggested that the only solution of the problem is to use an apparatus (not a respirator of the usual type) which will enable the miners to breathe directly the fresh uncontaminated surface atmosphere from the air-pressure pipes supplying their pneumatic drills.

Organic Analysis

Detection of Selenium in Organic Compounds and Soils. M. J. Horn. (*Ind. Eng. Chem., Anal. Ed.*, 1934, **6**, 34–35.)—The codeine colour test may be used for the detection of selenium after the destruction of organic matter by the Kjeldahl digestion method. One grm. of the dried sample is heated with 40 ml. of concentrated sulphuric acid and 0·2 grm. of mercuric oxide until a colourless liquid is obtained. To the cooled liquid, without dilution with water, 2 drops of a 3 per cent. aqueous solution of codeine sulphate solution are added with shaking and cooling. When selenium is present a green colour develops, rapidly changing to blue. The method may be applied to soils, when the cooled liquid after the digestion should be centrifuged, and the test made on the clear liquid. It is important that the codeine should be added to the cooled solution as soon after the digestion as possible, since when this is exposed to the air, moisture is absorbed by the sulphuric acid, and interferes. The amount of selenium may be determined approximately by comparison of the blue colour with that developed by solutions containing known amounts of selenium; the limit of sensitiveness is about 0·5 part per million of test solution. Selenium in amounts up to 20 parts per million was found in wheat grown on soil treated with sodium selenate. The possible effect of numerous elements on the method, as applied to soils, was tested, 0·2 mgrm. of the element, together with 5 grms. of soil, being digested with 50 ml. of sulphuric acid; only vanadium was found to interfere; 2 grms. of ferric sulphate, however, prevented the colour from forming. S. G. C.

New Method for the Micro-Determination of Methyl Alcohol in Presence of Large Quantities of Homologous Alcohols. M. Flanzy. (*Compt. rend.*, 1934, **198**, 94–97.)—This method is based on: (i) Transformation of the primary alcohols into the corresponding iodides and their subsequent regeneration by means of aqueous silver acetate; this gives the iodination index P. (ii) Oxidation in the cold of the regenerated alcohols, to obtain the oxidation index p. (iii) Establishment of an algebraic relation between P and p. Iodination is monomolecular in all cases, but whereas methyl alcohol is oxidised to carbon dioxide and water, its higher homologues yield the corresponding carboxylic acids. On these bases it is shown that, if x and y are the weights of methyl and ethyl (etc.) alcohols, respectively, in the solution analysed, P the weight of silver iodide formed and p the quantity of oxygen consumed, then

$$x = 62\left(\frac{p}{32} - \frac{P}{234{\cdot}8}\right) \text{ and } y = 138\left(\frac{P}{234{\cdot}8} - \frac{p}{48}\right).$$

The iodination is carried out in a Zeisel and Fanto apparatus (*Z. anal. Chem.*, 1903, **42**, 549) at 105 ± 5° C.; the washing flask contains aqueous calcium carbonate suspension at 50° C., and the iodides are collected in silver acetate solution, the condensing water being at 43° C.; 30 bubbles of carbon dioxide are passed per minute, and the distillation is continued for 1¼ hours. Under these conditions the methyl iodide passes completely, the ethyl iodide partly, and the other iodides not at all, into the silver acetate flask. This flask is heated under a reflux condenser for 2 hours to complete the reaction between the alkyl iodides and the silver acetate, the alcohols being then distilled into a 50-ml. flask and made up to volume.

To determine p, 5 ml. of this distillate are poured into 10 ml. of a solution containing 0·02 grm. of potassium dichromate and 5 ml. of sulphuric acid (66° Bé.). After 15 hours, when the oxidation is complete, the excess of dichromate is determined iodimetrically. A blank dichromate solution is also titrated after 15 hours; p is then calculated. To determine P, the residue in the silver acetate flask is dissolved in nitric acid and the solution boiled until the precipitated silver iodide becomes canary-yellow. This iodide is collected in a filtering crucible, washed, dried, and weighed (P). In solutions containing methyl and ethyl alcohols in the ratio of about 1 : 100, the error of the result is about 0·5 per cent.; for ratios between 1 : 1000 and 1 : 2000 the error is 5 to 10 per cent.

By means of this method the widespread occurrence of methyl alcohol has been discovered. For instance, contrary to the usual view, this alcohol is always present in fermented liquids. T. H. P.

Regularities in the Glyceride Structure of some Technically Important Vegetable Fatty Oils. T. P. Hilditch and E. C. Jones. (*J. Soc. Chem. Ind.*, **1934, 53,** 13–21T.)—The work described in detail in this paper has been undertaken to find a method for estimating fully unsaturated glycerides present in liquid fats. It has been found that if a fat whose unsaturated acids all belong to the C_{18} series is completely hydrogenated, it is possible, by systematic fractional crystallisation of the hydrogenated product, to obtain a series of least soluble fractions which contain all the tristearin present, accompanied only by palmito-distearins. The proportion of the distearins can be approximately estimated from the saponification equivalents of the fractions, and, consequently, the proportion of glycerides which were made up wholly of stearic, oleic, linolic or linolenic acids in the original fatty oil. The quantitative results, while less accurate than those obtained by direct determination of fully-saturated glycerides by the permanganate-acetone oxidation process, yet are reliable enough to show whether the distribution of fully unsaturated glycerides in the more liquid fats follows that of the fully-saturated components or not. The method applies only to those oils in which stearic acid is negligible, or at most forms only a few per cent. of the total fatty acids, but many important oils, such as olive, cotton-seed, linseed, etc., conform to the conditions. The original oil, hydrogenated as fully as possible, is crystallised systematically from appropriate solvents (ether, acetone and sometimes chloroform). So long as the palmito-distearins are the only glycerides accompanying the tristearin collected in the least soluble fractions, they can be approximately estimated, but, since the saponification equivalents of the two fractions show only a difference of 9·3, the calculation is only approximate. The setting points for such mixtures are, however, accurately known. Allowance must be made for the tri-C_{18} glycerides in the unsaturated residuum. To simplify calculations and permit of direct comparison between the original and hydrogenated material, molar percentages are used. The component fatty acids of the original oils studied, were estimated by the ester fractionation method, and were as follows:

TABLE I

(*a*) WEIGHT PERCENTAGES

	Cotton-seed	Soya bean	Lin-seed	Olive	Tea seed	Arachis nut
Myristic	3·3	0·6	0·2	1·1	0·3	—
Palmitic	19·9	7·0	5·4	9·7	7·6	8·2
Stearic (including arachidic from 0·3 to 0·9 per cent.)	1·9	5·8	3·5	1·9	1·4	3·4
Arachidic-lignoceric ..	—	—	—	—	—	6·1
Oleic	29·6			79·8	83·3	60·4
Linolic	45·3	86·6	90·3	7·5	7·4	21·9
Linolenic..	—			—	—	—

(*b*) MOLAR PERCENTAGES

	Cotton-seed	Soya bean	Lin-seed	Olive	Tea seed	Arachis nut
Myristic	4·0	0·7	0·3	1·4	0·4	—
Palmitic	21·4	7·7	5·9	10·6	8·3	9·0
Stearic	1·7	5·7	4·0	1·8	1·3	3·4
Arachidic-lignoceric ..	—	—	—	—	—	5·2
Oleic	28·7	85·9	89·8	78·7	82·6	60·4
Linolic	44·2			7·5	7·4	22·0
Linolenic	—			—	—	—

Table II shows in column I the oils that have been studied, and in column II the molar percentages of non-C_{18} acids, stearic and unsaturated C_{18} acids; column III shows the percentage of fully-saturated glycerides in the original oil, and column IV the extreme limits of the possible percentage of tri-C_{18} glycerides. The final column (V) gives the experimental molar percentage of tri-C_{18} glycerides obtained as a result of the quantitative fractional crystallisation of the hydrogenated fats.

TABLE II

I	II			III	IV	V
	Non-C_{18} Per cent.	Stearic Per cent.	Unsatd. C_{18} per cent.	Fully-saturated glycerides Per cent.	Limiting per cent. (mols.) for tri-C_{18} glycerides	Tri-C_{18} glycerides (found) Per cent.
Cotton-seed	25·4	1·7	72·9	—	24–62	24
Soya-bean	8·4	5·7	85·9	—	75–87	75
Linseed	6·2	4·0	89·8	—	81–91	83
Olive	12·0	1·8	86·2	2	68–83	57
Tea-seed	8·7	1·3	90·0	—	74–87	63
Ground-nut	14·2	3·4	82·4	—	57–79	Method inapplicable

D. G. H.

Tung Oil from *Aleurites Montana* and Specification Tests. L. A. Jordan. (*J. Soc. Chem. Ind.*, 1934, 53, 21–22T.)—Since tung oil from trees cultivated in different parts of the British Empire and the United States is about to come on the market, and since this oil will mostly be single-species oil, not blends (as is now so often the case with China oils that the discrimination between Hankow and Hong Kong oils has ceased to have real significance), specifications for such oils assume importance. *A. montana* appears to be better adapted for growing in hot climates; and since products made from this oil possess the high water resistance, gloss and durability associated with tung oil varnishes, it is unfortunate that a small proportion of suitable adulterant added to *A. Fordii* oil will give a product with the analytical characteristics of *A. montana* oil. A separate specification for *A. montana* is suggested, with the following lower limits in those characteristics which vary:—Sp.gr. at 15·5° C., 0·934; $n_D^{20^\circ}$, 1·5130; iodine value (Wijs), 155; heat test should not exceed 12 mins. and 30 per cent. extractive by the P.R.S. method (see above). Characteristic figures obtained for *A. montana* oils were as follows:—Chinese oil (*a*), Malay oil (*b*), and Ceylon oil (*c*): sp.gr. 15·5° C., (*a*) 0·9367, (*c*) 0·9364, 0·9367; $n_D^{20^\circ C}$, (*a*) 1·5169–1·5183, (*b*) 1·5135, (*c*) 1·5165, 1·5168;

iodine value (Wijs), (*a*) 162·2–165·0, (*b*) 162·7, (*c*) 163·0, 163·3; acid value, (*a*) 3·1–3·7, (*c*) 0·41, 0·45; heat test, P.R.S., (*a*) 10·3–11·0, (*b*) 11·5, (*c*) 11·0; extractive per cent., P.R.S., (*a*) 27·4–29·0, (*b*) 28·2, (*c*) 28·0. D. G. H.

Composition of an Aldobionic Acid from Flaxseed Mucilage. C. Niemann and K. P. Link. (*J. Biol. Chem.*, 1934, **104**, 205–206.)—Anderson and Crowder (*J. Amer. Chem. Soc.*, 1930, **52**, 3711) reported that flaxseed mucilage yields, on hydrolysis, an aldobionic acid composed of *l*-rhamnose and *d*-galacturonic acid. The free galacturonic acid was not isolated in the crystalline form, or as a crystalline derivative. The presence of *d*-galacturonic acid was inferred from oxidation studies. Since the occurrence of *l*-galactose in flaxseed mucilage has recently been reported by Anderson (*J. Biol. Chem.*, 1933, **100**, 249), it becomes desirable to know which stereoisomeric form of galacturonic acid is present in the aldobionic acid; only the *d* form has as yet been found in nature. The occurrence of the rather rare *l* form of galactose in the mucilage from the flaxseed raises the possibility that the corresponding *l* form of galacturonic acid might be present in the aldobionic acid. The data obtained and given establish conclusively that the *d* form of galacturonic acid is present in the aldobionic acid originally described by Anderson and Crowder. The presence of *l*-rhamnose as the sugar component of the aldobionic acid is also confirmed. P. H. P.

Mucilage from Slippery Elm Bark. E. Anderson. (*J. Biol. Chem.*, 1934, **104**, 163–170.)—Schirmer (*Arch. Pharm.*, 1912, **250**, 230; *Chem. Zentr.*, 1912, **2**, 195) reported that the mucilage from slippery elm bark contained 1·4 per cent. nitrogen, 12·18 per cent. of pentosan, 10·26 per cent. of methyl-pentosan, and 13·72 per cent. of fermentable sugars, calculated as glucose. He reported glucose, fructose and galactose among the sugars. The mucilage has now been prepared by the author from the bark of slippery elm, *Ulmus fulva*, and shown to be a mixture of two or more polyuronides, with varying amounts of calcium oxalate as an impurity; the latter is merely dissolved out of the bark together with the mucilage. The mucilage has been hydrolysed, and the presence of the following substances established: (*a*) galacturonic acid, (*b*) *l*-rhamnose, (*c*) *d*-galactose, and (*d*) a coloured non-saccharine X-body. In addition, there are indications of the presence of a pentose sugar, a methylated hexose sugar, and a methylated uronic acid. The polyuronides of the mucilage seem to be composed of a uronic acid combined with 2 molecules of simple sugars and an X-body in the following sequence. The uronic acid is combined, through its aldehyde group, with the methyl-pentose or pentose. The latter is combined through its aldehyde group with the hexose or methylated hexose. Finally, the hexose or methylated hexose is combined, through its aldehyde group, with the X-body. Contrary to the statement of Schirmer, neither glucose nor fructose was found. P. H. P.

Detection of *p*-Chlorobenzoic Acid in Presence of Benzoic Acid. F. Weiss. (*Z. Unters. Lebensm.*, 1934, **67**, 84–86.)—*p*-Chlorobenzoic acid (or its sodium salt), which is used as a food-preservative, generally in conjunction with benzoic acid (or its sodium salt), may be detected as follows:—Of the acid material (separated from the foodstuff either by steam-distillation or by extraction) 2 to 3 mgrms. are heated in a test-tube with 0·25 ml. of concentrated sulphuric acid and a few crystals of potassium nitrate for 20 minutes in a boiling water-bath. Two ml. of water and 2 ml. of ammonia solution are then added and mixed in by swirling, and about 1 ml. of hydroxylamine hydrochloride solution (2 grms. in 100 ml. of water) is added carefully so as to form an upper layer. Either at once or after a few minutes, according to the amount of the chloro-acid present, a more or less intense green zone appears. The reaction occurs, although more slowly, if the liquid is cooled before addition of the hydroxylamine solution. Owing to the low solubility of *p*-chlorobenzoic acid in water (1 in 5200 at 20° C.) it may be separated approximately quantitatively from benzoic acid by treating the separated mixed acids with water. T. H. P.

Detection of *p*-Phenylenediamine, in Presence of other Diamines, in Hair-dyes. C. Griebel and F. Weiss. (*Z. Unters. Lebensm.*, 1934, 67, 86–88.)—Since *p*-diaminoanisole and *p*-phenylenediamine show practically the same behaviour towards vanillin and hydrochloric acid, and the ferric chloride reaction of *p*-diaminoanisole is masked by the presence of *p*-toluylenediamine (ANALYST, 1933, 58, 417, 714), it becomes necessary, to detect *p*-phenylenediamine in hair-dye, to convert the amine into the dichloro-di-imine by treatment with hypochlorite. *p*-Diaminoanisole gives no crystallisable product with hypochlorite, but lowers considerably the decomposition point of the quinonedichloro-di-imine. It is, therefore, necessary to test the di-imine (after crystallisation from alcohol) by the vanillin and hydrochloride reaction: methylquinone-di-chlorodi-imine (from *p*-toluylenediamine) gives a persistent greenish-yellow coloration, whilst, with quinonedichloro-di-imine (from *p*-phenylenediamine), the similar coloration first obtained gradually changes, from the edge inwards, to brick-red with formation of precipitate. T. H. P.

Detection and Determination of Methyl Mercaptan and Carbon Disulphide in Air containing Hydrogen Sulphide. J. F. Reith. (*Rec. Trav. Chim. Pays-Bas*, 1934, 53, 18–23.)—The gas is passed in succession through two wash-bottles fitted with sintered-glass filters, and containing 20 ml. of 0·5 *N* sodium hydroxide solution; a drying-tube containing anhydrous calcium chloride; and 2 smaller wash-bottles containing 2 ml. of a fresh 5 per cent. solution of sodium hydroxide in absolute alcohol. *Methyl Mercaptan* (in the presence of up to 100 mgrms. of hydrogen sulphide):—The contents of the first two bottles, put together into one of them, are acidified with 4 ml. of 25 per cent. hydrochloric acid, and the bottle is then connected with two tubes (20 × 9 cm.) joined by a ground-glass joint, the first of which contains anhydrous calcium chloride, and the second about 20 grms. of finely-crystallised lead acetate, which should be packed in with glass wool so as to fill the tube; with the free end of the latter is connected a small wash-bottle containing 1 ml. of a fresh solution of 10 mgrms. of isatin in 100 ml. of concentrated sulphuric acid. When air is drawn through the system, any hydrogen sulphide is held by the lead acetate, whilst methyl mercaptan produces a grass-green colour with the isatin reagent. For a determination, two wash-bottles, each containing 1 ml. of a solution prepared by grinding 10 mgrms. of palladium chloride in a mortar with 1 ml. of 0·1 *N* sulphuric acid and 24 ml. of water, are substituted for the isatin reagent. The combined wash-liquors are then diluted to 5 ml. in a centrifuge tube, which is centrifuged in the same apparatus as mixtures of 2 ml. of the palladium chloride reagent and quantities of a standard solution of methyl mercaptan corresponding with 0, 0·005, 0·010, 0·020, etc., to 0·3 mgrm. of this substance, the total volume being always 5 ml. Since methyl mercaptan is volatile (b.pt. 5·8° C.), and is unstable when dissolved in a 5 per cent. solution of sodium hydroxide, the standard is prepared (freshly every day) by dissolving 31 mgrms. of crystalline lead mercaptide (*cf.* Borgstrom, Ellis and Reed, ANALYST, 1929, **54**, 767) in 4 ml. of 4 *N* acetic acid, 10 ml. of 0·1 *N* sulphuric acid being then added, the mixture filtered, and the filtrate diluted to 100 ml.; the actual mercaptan-content (about 0·1 mgrm. per ml.) may be checked by Rübner's method (*Arch. Hyg.*, 1893, **19**, 153). For 0·005 to 0·1 mgrm. of mercaptan the strength of the orange-brown colour of palladium mercaptide is used for comparison (error 0·01 mgrm.), whilst with larger quantities the precipitate must be weighed. *Carbon disulphide.*—This is obtained from the contents of the two small wash-bottles, which are rinsed into a beaker, first with 2·5 ml. (total) of 4 *N* acetic acid, and then with 10 ml. of 0·02 *N* copper acetate solution. After at least 2 hours the cuprous xanthogenate is collected on a sintered-glass crucible and washed with not more than 25 ml. of water. The precipitate is then treated with 0·5 ml. of 4 *N* acetic acid and 4 drops of freshly saturated bromine water, and, after 5 minutes, suction is applied; it is stopped when filtration is complete, and is continued 5 minutes after the addition of a further 4 drops of bromine water, the filter being finally washed with water until the filtrate amounts to 10 ml. This is then mixed with 0·5 ml. of a 5 per cent. solution of phenol and, after 5 minutes, 2·5 ml. of *N* potassium iodide solution are added, and the liberated iodine is titrated slowly with a 0·01 *N* solution of sodium thiosulphate, starch being used as indicator (1 ml. ≡ 1·5 mgrm. of carbon disulphide). The error is —0·01 to —0·04 mgrm. for from 0·03 to 1·31 mgrm., and —0·14 to —0·16 for from 2·61 to 13·05 mgrms. of carbon disulphide, but is so great as to invalidate the method for larger quantities; filtration should take place after 18 hours if less than 2·6 mgrms. is present. If a few drops of a copper solution are added, down to 0·01 mgrm. of carbon disulphide may be detected from the strong yellow colour developed in the above reaction (*cf.* Huff, ANALYST, 1926, **51**, 156; and Doran, *Ind. Eng. Chem., Anal. Ed.*, 1932, **4**, 98). The method has been applied in the investigation of the exhaustor gas drawn from the spinning rooms of an artificial silk factory.

J. G.

Platinised Silica-Gel as a Catalyst in Gas Analysis. II. Oxidation of the Methane Hydrocarbons. K. A. Kobe and E. B. Brookbank. (*Ind. Eng. Chem., Anal. Ed.*, 1934, **6**, 35–37.)—The oxidation of methane, ethane, propane, and butane over a commercial platinised silica-gel has been studied. The temperature below which the gases remained unoxidised under the conditions employed was 350° C. for methane, 230° C. for ethane, 130° C. for propane, and 120° C. for butane. Oxidation occurred at some 20° to 25° above these temperatures, but was not complete at 400° C. Hydrogen and carbon monoxide can be quantitatively oxidised over silica-gel at 300° C., and may thus be determined in the presence of methane, but not of the higher hydrocarbons, which suffer oxidation at this temperature.

S. G. C.

Inorganic Analysis

Quinaldinic Acid as an Analytical Reagent. P. Rây and M. K. Bose. (*Z. anal. Chem.*, 1933, **95**, 400–414.)—Solutions of copper, cadmium, zinc, uranyl, and ferrous salts yield insoluble precipitates with α-quinaldinic acid or its sodium salt. The dried copper salt has the formula $(C_{10}H_6NO_2)_2Cu,H_2O$, is very insoluble, and can be precipitated from acid solution. The precipitates are dried at 125° C. and weighed; the basic uranium salt is ignited to U_3O_8. The reagent may be applied to the separation of copper from lead, manganese, nickel, cobalt, and phosphoric and arsenic acids; and of zinc from manganese, magnesium, calcium, barium, and phosphoric acid. The reagent, which is somewhat expensive, may be recovered by precipitation as the copper salt and decomposition of the latter with hydrogen sulphide. Full directions for the procedure are given.

W. R. S.

Gravimetric and Volumetric Determination of Mercury as Mercurous Iodate. G. and P. Spacu. (*Z. anal. Chem.*, 1934, **96**, 30–34.)—The hot neutral or feebly acid solution of mercurous nitrate is treated, drop by drop, during agitation, with excess of potassium iodate solution (0·35 grm. per 100 ml.). The precipitate separates in the form of lustrous needles. After complete cooling (1 to 1½ hours) it is collected in a porous crucible, washed with water, alcohol and ether, dried *in vacuo*, and weighed (Hg factor, 0·5342). For the volumetric determination the mercury is precipitated with a known quantity of iodate, the excess being measured in the filtrate by adding iodide and dilute acid and titrating the liberated iodine with thiosulphate. The solubility of the precipitate was found to be 33·1 mgrms. per litre at 15·5° C. W. R. S.

Separation of Gold from Tellurium. V. Lehner, G. B. L. Smith and D. C. Knowles. (*Ind. Eng. Chem.*, *Anal. Ed.*, 1934, **6**, 43–45.)—The conditions have been investigated under which gold may be separated satisfactorily by precipitation with nitrous acid or ferrous sulphate; with nitrous acid, the p_H value of the solution should not be less than 1 to secure quantitative precipitation of gold. *Ferrous Sulphate Method.*—To the solution containing gold and tellurium (175 ml.), hydrochloric acid is added to provide a concentration of 1·5 to 2 per cent. of hydrogen chloride. The solution is heated to boiling, 1 to 1·5 grm. of ferrous sulphate is added, and the boiling is continued for 15 minutes. The precipitate of gold is filtered off on a Gooch crucible, washed with water, dried at 100° C., and weighed. In test-experiments with about 0·1 grm. each of gold and tellurium, the maximum error was —0·0002 grm. of gold. *Nitrous Acid Method.*—To the solution containing gold and tellurium chlorides (less than 275 ml. in volume and containing less than 1 to 1·5 per cent. of hydrochloric acid), 100 ml. of Rochelle salt solution (20 per cent.), followed by 25 ml. of sodium nitrite solution (4 per cent.) are added. The solution is kept until the gold has settled out; it is then brought to boiling, and the gold is filtered off and determined as above. In test-experiments with amounts of gold and tellurium from 0·14 to 0·19 grm. and 0·13 to 1·0 grm., respectively, the maximum error was —0·0004 grm. of gold. Sodium acetate was found to be less satisfactory as a buffering agent than Rochelle salt. *Determination of*

Gold and Tellurium in presence of each other.—The gold and tellurium are first precipitated together by the hydrazine and sulphur dioxide method of Lehner and Homberger (*J. Amer. Chem. Soc.*, 1908, 30, 387), double the quantities of reagents specified for this method being, however, used. The mixed precipitate is weighed, dissolved in *aqua regia*, and the solution is evaporated several times with hydrochloric acid; the gold is separated either by the nitrous acid method or the ferrous sulphate method; the weight of tellurium is obtained by difference. S. G. C.

Detection and Colorimetric Determination of Nickel in Cobalt Salts by means of Formaldoxime. G. Denigès. (*Bull. Soc. Pharm. Bordeaux*, 1932, 21, 106–107; *Ann. chim. anal.*, 1933, 15, 321–322.)—*Reagent.*—A mixture of 7 grms. of hydroxylamine hydrochloride, 3 grms. of trioxymethylene, and 15 ml. of water is gradually heated, and finally boiled until a clear solution is produced; it is then cooled. *Method.*—Into one of two test-tubes of the same dimensions are introduced 20 ml. of a solution of the cobalt salt to be tested (concentration, 0·05 grm. of cobalt per litre), and in the other tube is placed a similar volume of pure cobalt sulphate solution of the same strength. To both tubes are added 2 drops of reagent and 4 drops of 10 *N* sodium hydroxide solution, the liquids being well stirred after each addition. In the absence of nickel a straw-yellow colour is produced; in the presence of nickel the colour becomes more or less brown. It is stated that the amount of nickel may be determined colorimetrically by comparison of the colour with that of standards made by the addition of nickel to the pure cobalt solution. The sensitiveness of the method is not stated. S. G. C.

Colorimetric Determination of Magnesium. L. Debucquet and L. Velluz. (*Bull. Soc. Chim.*, 1933, 53, 1291–1292.)—The authors have described (*Bull. Soc. Chim.*, 1933, 53, 1290) a triple ferrocyanide of magnesium, calcium and hexamethylene-tetramine, a crystalline powder having the formula $3MgCaFe(CN)_6.4(CH_2)_6N_4.40H_2O$, and being somewhat unstable to air and light; it is very soluble in water, but almost insoluble in 10 to 20 per cent. aqueous hexamethylenetetramine solution. Magnesium may be precipitated in the form of this compound by the addition of a solution containing a specially prepared complex calcium ferrocyanide and hexamethylenetetramine. The magnesium may be determined, after collection of the precipitates, by a method involving colorimetric comparison of Prussian blue obtained by treatment of the aqueous solution of the precipitate with ferric chloride; the standard adopted for the comparison is the complex calcium ferrocyanide preparation, and the method is stated to apply only to amounts of magnesium close to 0·1 mgrm. For details, reference to the original paper should be made. S. G. C.

Colorimetric Determination of Potassium. S. N. Rosanow and W. A. Kasarinowa. (*Z. anal. Chem.*, 1934, 96, 26–29.)—The following method was evolved for rapid serial determinations of potassium in soils:—The solution (1 ml.), free from ammonium salts and containing 0·025 to 0·1 mgrm. of potash, is acidified with 2 drops of 3 per cent. acetic acid, and treated with 1 ml. of sodium cobaltinitrite reagent in a centrifuge cylinder. After 4 hours' standing the precipitate is centrifuged for 15 to 20 minutes, the clear liquid is syphoned off, and the precipitate is washed by 5 minutes' centrifuging with 2-ml. portions of water repeated until the washings are quite colourless (6 to 7 times). The precipitate is then digested with 5 ml. of 0·1 *N* sodium hydroxide solution on the water-bath; the alkaline liquid is diluted to 50 ml. in a graduated 100-ml. flask, and treated with 2 ml. of a mixture of equal parts of 10 per cent. hydrochloric acid and phenol-sulphanilic acid reagent. After 15 minutes the liquid is made alkaline with 10 per cent. ammonia, and the volume is adjusted. The tint is matched against that of a standard nitrite solution (0·2709 grm. of potassium nitrite per litre; 1 volume of this solution diluted with 9 of water; 1 ml. = 0·005 mgrm. of K_2O) treated in the same manner. The reagent is made up of 1 grm. of sulphanilic acid dissolved in 100 ml. of warm saturated ammonium chloride solution, and 1·5 grm. of phenol dissolved in 100 ml. of water; it keeps in the dark for 2 to 3 weeks. The potassium precipitate must always be produced under uniform conditions.

W. R. S.

Colorimetric Determination of Traces of Fluorine. L. Szegoe and B. Cassoni. (*Giorn. Chim. Ind. Appl.*, 1933, 15, 599–602.)—The two methods described are based on the distillation of silicon tetrafluoride and hydrofluosilicic acid, respectively, followed by colorimetric estimation in a Pulfrich photometer. The first procedure is inapplicable in presence of an appreciable amount of colloidal silica, which results either in the formation of the non-volatile $SiOF_2$ or in adsorption of the fluorine ion, this being liberated only after greatly prolonged distillation. The second method may be used when colloidal silica is present, as is the case in the ash of animal or vegetable tissues.

(i) The weighed material, mixed with lime water (about 1 per cent. of CaO on the sample), is dried and carefully incinerated at a temperature not exceeding 550° C. The residue is mixed with 6 parts of sodium and potassium carbonate mixture and 1 part of silica, and the whole is fused and afterwards extracted with hot water and filtered. The filtrate is treated with ammonium carbonate to separate the silica, which is removed by filtration. The clear solution is treated first with 0·3 to 0·4 grm. of sodium sulphate and then with barium chloride. After some hours the precipitate is filtered off, dried, mixed with pure powdered quartz, and transferred to a distillation flask provided with a gas-delivery tube and connected with a 10-bulb absorption tube containing about 10 ml. of water. After addition of about 50 ml. of 98·5 per cent. sulphuric acid to the flask, the temperature is raised rapidly to 200° C. and then slowly to 300° C., which is maintained for 2 to 3 hours; during the distillation a slow current of dry air is passed.

(ii) In this method use is made of the calcined mixture of lime and material, or, for fluorides not attacked by acid, of the material obtained by fusion with alkali and silica (see above). This is placed in a distilling flask (50 to 100 ml.) closed with a two-holed rubber stopper carrying a thermometer and a tapped funnel, both of these reaching the liquid after the flask is charged. A 5-ml. excess of perchloric acid (60 per cent.) over the amount required to neutralise the mixture is added from the funnel, and sufficient water is then introduced to give the liquid a b.pt. between 100° and 110° C. Distillation is continued until the temperature reaches 135° C., this being maintained by gradual addition of water. From 50 to 100 ml. or, in presence of colloidal silica, 500 ml. of distillate are collected. The distillate is neutralised with sodium hydroxide and concentrated on a water-bath.

The solution obtained in either way is placed in a 50-ml. flask and, after addition of 5 ml. of M/40 titanium sulphate solution and 2 ml. of 3 per cent. hydrogen peroxide solution (fluorine-free), made up to volume. A solution containing only the titanium sulphate and hydrogen peroxide in these concentrations is prepared, and the colours of the two are compared in a Pulfrich photometer, 2-cm. depths of liquid being used. From the value of the transparency D, read off when the filter S50 (or S47) is employed, the concentration of fluorine in the solution is determined by graphic interpolation of the function $1/d.\log 1/D$ on curves prepared from the following table:

Mgrms. F. per 50 ml.	D(S50)	$\frac{1}{d}.\log\frac{1}{D}$	D(S47)	$\frac{1}{d}.\log\frac{1}{D}$
0·095	95·1	0·011	92·0	0·018
0·190	90·5	0·022	84·0	0·037
0·38	81·5	0·044	71·0	0·074
0·57	74·5	0·066	58·8	0·115
0·76	74·5*	0·066*	58·8*	0·115*
0·95	61·0	0·107	41·7	0·190
1·90	41·0	0·194	21·7	0·332
2·85	31·0	0·254	13·5	0·435
3·80	26·0	0·292	10·1	0·498
5·70	22·0	0·329	7·6	0·550

* As in original, but apparently erroneous.—*Abstractor.*

By method (i) 4·64, 2·68, 1·44, 4·53 (+0·5 grm. H_3BO_3) and 1·90 (+3 grms. of plant ash) mgrms. of fluorine as calcium fluoride gave 4·27, 2·42, 1·38, 4·18, and 0·44 mgrms., respectively. By method (ii) 3·80 and 0·95 mgrms. of fluorine as potassium fluoride gave 3·90 and 0·90 mgrms., respectively, and 1·90 mgrms. as calcium fluoride (+3 grms. of plant ash) gave 1·82 mgrms.

The titanium sulphate solution is prepared by heating 0·6003 grm. of pure potassium fluorotitanate with 20 ml. of 50 per cent. sulphuric acid in a platinum dish until copious white fumes appear, cooling, adding water and again heating to fuming point; after a second dilution and heating, the liquid is made up to 100 ml. with water. (*Cf.* Wichmann and Dahl, ANALYST, 1934, 132.)

T. H. P.

Volumetric Method for the Determination of Sulphate. V. R. Damerell and H. H. Strater. (*Ind. Eng. Chem., Anal. Ed.*, 1934, **6**, 19–21.)—Sulphate may be titrated with barium chloride, mercuric nitrate being used as an external "spot-plate" indicator; the presence of soluble sulphate is shown by the formation of yellow-coloured basic mercuric sulphate. The following method was used in test-experiments: To the sulphate solution (100 ml., 0·005 to 0·02 *M*) was added barium chloride solution (0·02 to 0·07 *M*) from a burette, and, from time to time, one drop of the solution was withdrawn, and added to one drop of mercuric nitrate solution (see below) in a depression on a spot-tile. The yellow colour produced by the indicator was compared with that of 4 drops of a standard coloured solution placed in a neighbouring depression in the tile (the colour standard was a freshly-prepared mixture of 1 volume of a solution containing 4·3 grms. of potassium sulphate and 0·2 grm. of potassium dichromate per litre and 1 volume of a solution of 8 grms. of barium chloride crystals per litre). The time taken for the appearance of the yellow colour increased as the end-point of the titration was approached, and, at the stage at which several seconds were required for the colour to exceed that of the standard, the amount of solution added to the 1 drop of mercuric nitrate indicator was increased to 3 or more drops. The end-point of the titration was taken to be when a period of 30 seconds was required for the yellow colour produced with the indicator to equal in intensity that of the standard. The end-point thus obtained did not exactly correspond with the stoichiometric equivalence point; thus, when 0·621 *M* barium chloride solution was added to 100 ml. of 0·0125 *M* potassium sulphate solution, 19·16 ml. were required, whereas the stoichiometric amount would be 20·13 ml.; it is, therefore, recommended that the barium chloride solution be standardised against a pure sulphate. The sulphate solution should be neutral or faintly acid. The method is subject to interference by numerous salts, and is thus restricted to comparatively pure sulphate solutions. Appreciable errors were caused, for example, by the presence of more than about 0·3 grm. of sodium chloride; nitrates, ammonium salts, and ions which give precipitates with mercuric nitrate or with barium chloride under the conditions employed (*e.g.* phosphate, tartrate, etc.), interfere. *Preparation of Mercuric Nitrate Indicator.*—A mixture of 20 grms. of mercuric oxide, 10 ml. of nitric acid (sp.gr. 1·42) and 8 ml. of water was kept stirred for some time, resulting in a very turbid liquid; this was filtered, and 6 ml. of water were added. The solution was kept for several hours before use, during which time a light-coloured crystalline precipitate of basic mercuric nitrate separated out; this precipitate was taken as a satisfactory indication of low acidity of the indicator, a condition essential to the success of the method. S. G. C.

Volumetric Determination of Chlorate. K. Glew. (*Z. anal. Chem.*, 1933, **95**, 385–392.)—The solution of the chlorate (about 0·25 grm.) in 100 to 150 ml. of *N* sulphuric acid is treated with excess of 0·1 *N* arsenite solution. The air is expelled from the flask by addition of 2 to 3 grms. of sodium bicarbonate in several portions. The solution is then treated with 3 drops of 0·01 *M* osmium tetroxide solution and 3 drops of 0·01 *M* ferroin (ferro-*o*-phenanthrolin), and titrated, drop by drop, with 0·1 *N* ceric sulphate solution, admission of air being avoided. As a check, 5 ml. of the 0·1 *N* arsenite solution may be added to the titrated liquid; these should consume another 5 ml. of 0·1 *N* ceric solution. The procedure gave positive errors of about 0·2 per cent. The presence of large amounts of perchlorate and small quantities of chloride is immaterial (*cf.* ANALYST, 1934,).

W. R. S.

Microchemical

Method of Stirring during Micro-electrolysis. A. Okáč. (*Mikrochem.*, 1933, **12**, 205–210.)—For micro-electrolysis in complex ammoniacal solutions, Pregl's method of stirring by gentle boiling is unsuitable, and, without stirring, the time taken for metallic deposition is inconveniently long. Two methods of stirring, by passing small bubbles of gas through the cell, are described: (i) The electrolysis vessel is similar to the Pregl type (8 cm. high and 1·5 to 1·8 cm. in diameter), except that there is a side-tube above the surface of the liquid to facilitate emptying and cleaning. The Pregl type of cathode is used. The anode passes down inside a narrow tube until it reaches the surface of the liquid, when it passes outside the tube (which is drawn out to a capillary of 1·5 to 2 mm. in diameter and ends in a spherical knob containing exit-holes for the gas). Carbon dioxide from the excess pressure of a Kipp's apparatus (only 0·9 cm. of mercury) is a suitable gas to use; with the addition of a three-way tap, the gas inlet tube may also be used for sucking out the liquid from the vessel. (ii) The electrolysis vessel is a small funnel of the same dimensions as type (i) with a fritted Jena-glass filter above the constriction and a glass tap below. The Pregl type of electrodes rest on the glass filter, through which the bubbles of gas at a pressure of about 1·8 cm. of mercury pass upwards. The vessel must be covered with a cover-glass to prevent splashing. Type (i) is the more suitable for accurate analytical work.

J. W. B.

Apparatus for Micro-electrolysis. H. Brantner and F. Hecht. (*Mikrochem.*, 1934, 14, 27–29.)—For the micro-electrolysis, a platinum crucible is used as the cathode. The volume of liquid ranges from 2 to 12 ml., and the crucible size may be varied accordingly. External contact with the source of current is made through an aluminium block, and the platinum crucible is fitted into a hole in the block, which is lined with thin platinum foil to prevent contamination of the electrode. The aluminium block can be heated with a micro-burner, and the electrolysis carried out at any desired temperature. The anode is in the shape of an inverted T, and a hook at the top hangs over a loop of platinum wire passing through the glass and making contact with mercury in a vertical glass tube; the whole is enclosed in an outer tube ending in a bulb which fits over the top of the cathode crucible, to prevent splashing. There is a small hole in the bottom of the bulb, through which the anode can be placed on the hook. A narrow bent-glass tube, reaching to the bottom of the crucible, facilitates cleaning; it may be attached to the pump for emptying the vessel, and the wash-liquid may be introduced through it. The apparatus is suitable for the determination of both anodic and cathodic depositions, and the aluminium heating-block is useful for drying the cathode (or anode) before weighing. J. W. B.

NOTE BY ABSTRACTOR.—This method is essentially the same in principle as one used by Emich in 1915.

Micro-electrolytic Determination of Lead. H. Brantner and F. Hecht. (*Mikrochem.*, 1934, 14, 27–29.)—The apparatus described by the authors (see preceding abstract) is used. The lead is deposited on the anode without the addition of copper. The deposited lead peroxide is not weighed as such, as the percentage of lead is not sufficiently constant, but is dissolved in 6 drops of water, 6 drops of nitric acid and 1 drop of 1 : 5 (by volume) hydrogen peroxide, and evaporated with 2 drops of concentrated sulphuric acid, after which it is ignited for ten minutes at 600° C. and weighed as lead sulphate on the micro-balance.

Conditions must be kept very constant for complete deposition of the lead. For weights of lead between 0·5 and 5 mgrms. good results were obtained, with less than 1 per cent. error, when the nitric acid concentration was 13 per cent., and the electrolysis was carried out for 45 to 55 minutes at 60° to 70° C., the current strength being 0·3 amp., which was raised to 0·5 amp. during the last 10 minutes of electrolysis. The addition of urea just before the end of the electrolysis has no beneficial effect under these conditions. The total surface area of the platinum crucible used for electrolysis was 20 sq. cm. If the solution is required for further analysis, as in the analysis of minerals, it is drawn off by suction into a suitable vessel by means of the bent-glass tube dipping through the liquid to the bottom of the crucible; this tube is closed with a rubber tube and clip during the electrolysis.

J. W. B.

Micro-determination of Magnesium by means of Hydroxyquinoline. G. Glomaud. (*J. Pharm. Chim.*, 1934, 19, 14–29.)—The hydroxyquinoline method with the bromate volumetric procedure of Berg (*Pharm. Zeit.*, 1926, 71, 1542) has been adapted to the determination of magnesium on the micro-scale. The *reagent solutions* are:—(i) *Standard bromide·bromate solution* (*N*/10), containing 2·785 grms. of potassium bromate, 50 grms. of potassium bromide and water to 1000 ml. (ii) *Starch solution*, made by mixing 2 grms. of pure potato starch with 100 ml. of cold water and 50 grms. of mercuric chloride, and pouring the mixture gradually into a litre of boiling water, which is kept boiling for 30 to 40 minutes. When cold, the solution is diluted to 1 litre; it will keep for several months. (iii) 8-*Hydroxyquinoline solution* : a 2 per cent. solution in 95 per cent. alcohol. (iv) A 10 per cent. (by vol.) solution of hydrochloric acid (approx. *N*). (v) A 40 per cent. solution of potassium bromide. (vi) A 20 per cent. solution of potassium iodide. (vii) A standard solution of sodium thiosulphate.

I. *Volumetric Determination of Hydroxyquinoline.*—Twenty to 30 ml. of the hydrochloric acid solution, 5 to 10 ml. of the potassium bromide solution, and an excess of the bromide-bromate solution are added to the hydroxyquinoline in a conical flask, which is then stoppered and shaken gently for 20 to 30 seconds, when excess of potassium iodide is added. The liberated iodine is titrated with *N*/5, *N*/20, or *N*/50 sodium thiosulphate solution. The method may be used to determine as little as 0·2 mgrm. of hydroxyquinoline, with maximum error of 3 per cent. II. *Precipitation of Magnesium.*—Ten ml. of magnesium solution in a 60-ml. conical flask are treated with the reagent in very slight excess, and the solution is made strongly alkaline by the addition of 1 ml. of ammonia solution. The flask is closed with a plug of cotton wool, and placed on the water-bath for five minutes, and its contents are filtered hot through a 12G4 Jena-glass filter, with the aid of suction. The precipitate is washed 3 times with 5 ml. of 10 per cent. ammonia solution, and then dissolved in 10 to 15 ml. of the dilute hydrochloric acid solution, and the hydroxyquinoline is determined as described in (I). The method has been tested for amounts of magnesium varying from 0·05 to 5 mgrms., and is satisfactory for amounts as small as 0·1 mgrm., errors of less than 3 per cent. being obtained. III. *Determination of Magnesium in Biological Extracts.*—This implies the determination of magnesium in the presence of phosphates and calcium. Phosphates do not interfere if the hydroxyquinoline reagent is added before the ammonia. Very low results are obtained for magnesium in the presence of more than 5 times the weight of calcium, when the calcium is removed by one precipitation either as calcium oxalate or calcium tungstate. Good results are obtained in the determination of magnesium in the presence of 10 to 15 times the amount of calcium, when the calcium is precipitated as oxalate, but not removed from the mixture. About 10 ml. of the magnesium solution are treated in a 30-ml. conical flask first with the hydroxyquinoline reagent, then with sufficient ammonium oxalate to precipitate the calcium, and with 2 ml. of ammonia solution. The flask is stoppered as before and heated for 5 minutes on the water-bath, the liquid is filtered, and the hydroxyquinoline is determined as described above; the oxalate does not interfere. J. W. B.

Micro-Method for the Determination of Ammonia. K. Linderstrøm-Lang and H. Holter. (*Compt. rend. Lab. Carlsberg*, 1933, 19, [20], 1–8.)—The method is suitable for the determination of very small amounts of ammonia (0·00019 to 0·028 mgrm. of nitrogen) in a small volume of liquid, *e.g.* in the determination of the hydrolysis of urea by urease. A liquid film method similar to that employed by the authors for the determination of sugars is used (*cf.* ANALYST, 1933, 58, 568). A similar paraffined reaction-vessel, 3·8 mm. in internal, 6 mm. in external diameter, and 25 mm. high, is also used. The solution under examination is introduced by means of a capillary pipette to the bottom of the vessel; the volume should not exceed 14 c.mm. A small needle of metal, enclosed in a glass capillary, which is to act as the stirrer, is added, the vessel is held horizontally, and a drop of 2 N sodium hydroxide solution (about 7 c.mm.) is placed about 5 mm. from the bottom by means of a capillary pipette with a curved tip. Next a film (about 35 c.mm.) of water free from carbon dioxide is added about 5 mm. from the top of the vessel, which is then raised to the vertical position, thus causing the drop of sodium hydroxide solution to run down and mix with the liquid under examination. Finally, 7 c.mm. of hydrochloric acid of suitable strength containing bromocresol purple as indicator are pipetted into the aqueous layer. The strength of acid used is 0·3 N, titrated back with $N/10$ alkali for 0·028–0·0028 mgrm. of nitrogen; for lower nitrogen-content 0·03 N acid is used and titrated back with $N/100$ sodium borate (Sørensen), as the strength of $N/100$ sodium hydroxide solution did not remain sufficiently constant for very small titrations. The indicator solution consists of 0·4 grm. of bromocresol purple dissolved in 1 litre of water and adjusted to p_H 5·9; 50 ml. of the acid used contain 10 ml. of this indicator solution, and both are added together. After the addition of the acid the sodium hydroxide solution and liquid under examination are mixed by means of the metal stirrer, which is set in motion by an electro-magnet (Linderstrøm-Lang and Holter, *Compt. rend. Lab. Carlsberg*, 1932, 19, [4]). The vessel is then stoppered by means of a rubber tube and glass tube, open at the lower end and drawn out to a tip and sealed at the other end, and the vessel is half immersed in a thermostat at 40° C. for 3 to 5 hours, so that the ammonia distils into the acid layer. When the distillation is complete a metal stirrer is put into the acid layer, and agitated by means of the electro-magnet, and the excess of acid is titrated against alkali or borate to p_H 5·9, the micro-burette previously described (ANALYST, 1933, 58, 568) being used. The accuracy of the determinations is about 0·1 c.mm. of $N/100$ borate, corresponding with 0·000014 mgrm. of nitrogen, and the error of the mean values is considerably less. J. W. B.

Errata: February issue, p. 127.—The figure referred to in line 13 is Fig. 2 (not Fig. 1) in the original paper. p. 136.—The figure referred to in line 25 is Fig. 2 (not Fig. 1) in the original paper.

Reviews

ALLEN'S COMMERCIAL ORGANIC ANALYSIS. Fifth Edition. Vol. X. Edited by C. AINSWORTH MITCHELL, M.A., D.Sc., F.I.C. Pp. 817. London: J. & A. Churchill. 1933. Price 32s.

"Let us praise famous men and our fathers which begat us." One such was Alfred Henry Allen amongst analysts. He could have no more fitting memorial than the continuance and growth of *Commercial Organic Analysis*, the fifth edition of which is completed by the publication of this tenth volume.

In reviewing the first edition, which occupied only two volumes (ANALYST, 1882, 7, 43), Wigner and Muter said: "In a word, no modern analyst's library can be considered complete without a copy"; words which have been proved to be correct by the appearance of successive editions in England and in America up to the present time. And if the new edition differs in style from the earlier products of Allen's own pen, it is largely because it is no longer possible for one man to compass all the detail of different branches of the subject with which modern analysts have to deal. Within the wide purview of the title there are few subjects, on which help is not to be found in the 7000 pages of these volumes.

The first and second editions from Allen's own pen showed his unrivalled flair for accurate and concise description either of substance or method. It is no longer possible for one man himself to write the whole of "Allen," but it would be ungenerous to fail to refer to the skill of the Editor, Dr. C. A. Mitchell, who, besides writing much himself, has so marshalled his contributors—over 70 in all—as to produce such a comprehensive and harmonious whole. Few could have done it, and none better.

Volume X is to some extent an after-thought. It includes branches of protein chemistry which could not be pressed into Vol. IX, and a number of subjects which have not hitherto been included in "Allen"—Vitamins, Hormones, Woods and Charcoals, Pectins, and a number of smaller, though no less important matters. Last, but not least, is a comprehensive index of the whole series, due to Miss Elliott, which greatly enhances the usefulness of the work.

Like the earlier volumes, this one is much more than a mere exposition of analytical method. There is a great deal of organic and physiological chemistry in it, and the various processes are so prefaced with exposition of underlying theory as to give a clear understanding of the subject and its limitations—a point of particular importance in connection with the matters contained in this volume.

Considering the detailed contents of this part, there is, first, an excellent section by Gardner and Buckmaster on haemoglobin, which is thorough and informative, though it might well have included the best methods for the determination of blood sugar and Southgate's method for alcohol in the blood for forensic purposes. Then follows a discussion of albuminoids by J. Alexander, which includes gelatins, isinglass, glues for various technical purposes and, incidentally, a method for determining dextrin in glue mixtures. Structural Proteins (by Dreaper and Marriott) treats of animal fibres, silks—natural and artificial—hair, hair dyes, furs and wool.

The next sections diverge considerably in character from normal chemical analysis. They deal with matters physiological and therapeutic—Vitamins by Drummond and Coward, and Hormones by Culhane and Underhill. The names of the authors are sufficient warranty for the excellence of their work, and it is not their fault that they follow so closely in the wake of new discovery that some statements made yesterday are not correct to-day. For example, the formula of vitamin *A* is given on p. 290; a note on p. 291 gives another formula, and now in 1934 yet a third is thought correct. These sections describe in careful detail methods for biological assay of each vitamin and give important instruction or warning on the pitfalls of animal experimentation. Unfortunately, the chemical titration of vitamin *C* had not been elaborated when this section was written, thus affording another instance of how quickly new matter arises in this field. Under hormones are described insulin, adrenaline, thyroxine and its derivatives, and their assay; also the testing of gland preparations and the physiological (or should one say surgical?) assay of oestrin, corpus luteum, testicular hormone and other bodies; these are explained in detail, though there will be few analysts who would undertake such work—a consideration which affords food for thought, in view of the inclusion of some of them in the B.P.

Lastly, we return to the more strictly chemical field, for there come sections on woods and charcoals by Maby and on pectic substances by Buston. These open up new fields of chemical investigation for the specialist, though much in Buston's section is of importance also to the food chemist and to the Public Analyst.

The whole is a treatise valuable—indeed invaluable—to the practising analyst, and worthy to rank with the "Allen" of bygone days; that is sufficient praise.

H. E. Cox

METALLURGICAL ANALYSIS BY THE SPECTROGRAPH. By D. M. SMITH. Published by The British Non-Ferrous Metals Research Association. Pp. 100 and Bibliography. Eight text-figures and 10 plates. 1933. Price 10/6.

Those associated with the development of spectro-analytical methods fully recognise the extreme improbability that such methods will ever replace orthodox chemical methods in the accurate determination of major constituents. They have, however, felt justified in claiming that spectrographic methods have a very definite sphere of application in the detection and estimation of minor constituents and traces of impurity, and that they possess special advantages in the routine examination of metallurgical products.

Some eight years ago Mr. D. M. Smith was engaged by the British Non-Ferrous Metals Research Association to investigate the potentialities of spectrographic methods in the estimation of impurities in various non-ferrous metals and alloys. Initial tests more than justified the continuance of the investigation, and reports upon it were issued at intervals to members of the Association. In a somewhat condensed form, the information contained in these reports is now given wider publicity in the present monograph.

Precise details are given for the spectrographic analysis of zinc, tin, lead, and copper, for all the commonly occurring impurities. The percentage range of estimation naturally varies with the spectroscopic sensitivity of any given elementary impurity, but, in general, it may be said to vary from 0·0005–0·5 per cent. to 0·01–1·0 per cent. One photographed spectrum (spectrogram) normally suffices for the determination of all impurities. The quantitative method most frequently adopted by the author is the internal standard method of Gerlach, the data being given in a tabular form originated by Brownsdon and van Someren. Other quantitative methods described include the simple "comparison sample" method and the logarithmic sector method, the application of the latter being illustrated by the determination of tin in lead over a range of from 0·1 to 3·0 per cent. The degree of accuracy attained by the author was, in general, ± 10 per cent. of the absolute value, which, for quantities under 1 per cent., should prove ample for the control of production. When samples are examined in batches of ten or so, the time required for complete analysis averages about ten minutes per sample.

The text is accompanied by a number of excellent reproductions of spectrograms, while the addition of several preliminary chapters on general principles and technique will enable those less well acquainted with quantitative spectrum analysis to follow the book more readily.

Few persons have had wider experience in the metallurgical applications of the spectrograph than Mr. Smith, and his monograph should find a ready welcome, among both those at present employing spectrographic methods and those contemplating their adoption.

C. STANSFIELD HITCHEN

FLUORESCENCE ANALYSIS IN ULTRA-VIOLET LIGHT. By J. A. RADLEY, B.Sc., A.I.C., and JULIUS GRANT, Ph.D., M.Sc., F.I.C. Pp. xi+219. London: Chapman & Hall. 1933. Price 15s. net.

The application of the term "analysis" to a large proportion of the contents of this book is somewhat of a misnomer, although the authors are only following the precedent set by Danckwortt and other Continental authorities. Whilst the restricted title may not be widely misunderstood, it does not do justice to the scope of the book, which is also concerned with other than the strictly analytical aspects of the subject. The work is, in fact, an attempt to give a practical survey of all the scientific uses of ultra-violet light in the examination of materials, and to summarise critically the extensive literature scattered over a wide range of scientific journals. Many of the recorded results have been checked by the authors, and where this was not possible they have wisely given even contradictory results, so that those who consult the book may have all available data.

The volume is divided into two parts: the first dealing with the theory and practice of fluorescence examination, and the second with its special applications. In the first part, sub-divided into five chapters, a description is given of the theory and practice of the process, including an account of the various forms of ultra-violet lamps, the use of spectacles and filters, and the measurement of the intensity of ultra-violet light. There is also a useful section on photographic technique, with full references to published methods, although to some extent the reader is left to work out his own procedure. By the way, the authors constantly refer to photographs in ultra-violet light as "luminograms," although that is the registered name of fluorescence photographs taken by a secret process.

The second part of the book is divided into nineteen chapters arranged in the alphabetical order of their subject-matter, such as agriculture, botany, drugs, foods, medical and biological science, organic chemistry, paper, rubber, textiles, water and sewage, etc. There are also interesting chapters on the use of ultra-violet light for such specialised purposes as legal work and museum work, with abstracts of the various papers published on the subjects and complete lists of references. The work concludes with some excellent examples of "luminograms" and other photographs, and with full subject- and author-indexes.

Obviously the book has entailed a very large amount of work and the mental digestion of an immense amount of published material, and the authors may be warmly congratulated on the result. The ultra-violet lamp has now become almost indispensable to the analyst, and this is by far the best guide to its use yet published.

EDITOR

Pharmacopoeia Commission

THE British Pharmacopoeia, which was published in September, 1932, has been on the whole favourably received, but has necessarily led to considerable criticism of detail.

The new Pharmacopoeia Commission, which took office in October, 1933, are now engaged in dealing with these criticisms, in investigating disputed points, and in collecting the material required for revision. Expert Sub-Committees have been formed to deal with different aspects of the work.

It is proposed that a complete revision of the Pharmacopoeia shall be made during the next seven years, and that a new Pharmacopoeia shall be issued in 1941.

It is proposed also to publish an Addendum in 1936. This Addendum will contain any alterations in the standards and tests of the Pharmacopoeia which experience shall have shown to be advisable, and will include descriptions of, and standards for, new drugs.

The Pharmacopoeia Commission are desirous of the opportunity of considering comments upon the standards and tests for the substances included in the Pharmacopoeia, and they invite manufacturers, pharmacists and others to send to the Secretary of the Pharmacopoeia Commission, 44, Hallam Street, W.1, any representations which they wish the Commission to consider.

March 5th, 1934.

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APRIL, 1934 Vol. 59, No. 697

THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

An Ordinary Meeting of the Society was held at the Chemical Society's Rooms, Burlington House, on Friday, March 2nd, at 3 p.m., the President, Mr. F. W. F. Arnaud, being in the chair.

Certificates were read in favour of Ronald Andrew Balding, Bertram Eastwood Dixon, M.Sc., A.I.C., A.C.G.F.C., Arthur Glover, M.Sc., A.I.C., Ralph Gordon Harry, A.I.C., Reginald Milton, B.Sc., Roy Warren Watridge, B.Sc., F.I.C.

The following were elected Members of the Society:—Donald Burton, M.B.E., D.Sc., F.I.C., Arthur Sereld Houghton, M.Sc., F.I.C., Homi Ruttonji Nanji, B.Sc., Ph.D., D.I.C., A.I.C., Harold Overton, B.Sc., John Milner Russell, B.Sc., Walter Frederick Waters, B.Sc., A.I.C.

The Annual General Meeting of the Society then followed, when Special Resolutions were passed for the alteration of certain Articles of Association of the Society, and the President delivered his Presidential Address.

The following were elected as Officers and Council for the year 1934:—

President.—John Evans, F.I.C.

Past-Presidents serving on the Council.—F. W. F. Arnaud, E. Richards Bolton, J. T. Dunn, Bernard Dyer, Edward Hinks, P. A. Ellis Richards, G. Rudd Thompson, J. Augustus Voelcker.

Vice-Presidents.—L. Eynon, S. E. Melling, A. More, W. H. Roberts.

Honorary Treasurer.—E. B. Hughes.

Honorary Secretary.—G. Roche Lynch.

Other Members of Council.—A. L. Bacharach, H. E. Cox, F. G. Edmed, E. M. Hawkins, L. H. Lampitt, H. Lowe, C. H. Manley, C. E. Sage, J. R. Stubbs, J. F. Tocher, E. Voelcker.

Anniversary Dinner

THE Society of Public Analysts was founded in August, 1874, and its first Annual Meeting was held in February, 1875. On Friday, March 2nd, 1934, the Society (whose scope and title were extended in 1907 to include analysts other than Public Analysts) held a dinner at the Trocadero Restaurant to commemorate the sixtieth year of its foundation.

The members and guests, who numbered 126, were received by the President, Mr. F. W. F. Arnaud, F.I.C., and Mrs. Arnaud, and he afterwards took the chair at the dinner.

The guests of the Society included the Rt. Hon. Lord Cornwallis, C.B.E., D.L., J.P.; Sir Isidore Salmon, C.B.E., D.L., J.P., M.P.; Sir Robert Robertson, K.B.E., D.Sc., F.I.C., F.R.S. (Government Chemist); Sir William J. Pope, K.B.E., D.Sc., LL.D., F.I.C., F.R.S.; Professor J. F. Thorpe, C.B.E., D.Sc., F.I.C., F.R.S. (President of the Institute of Chemistry); Professor G. T. Morgan, O.B.E., D.Sc., F.I.C., A.R.C.S., F.R.S. (President of the Chemical Society); Mr. William Macnab, C.B.E., F.I.C., M.I.Chem.E. (President of the Institution of Chemical Engineers); Sir Bernard Spilsbury, M.A., M.B., B.Ch., F.R.C.P. (President of the Medico-Legal Society); Dr. Charles Porter, M.D., M.R.C.P., M.O.H. (President of the Society of Medical Officers of Health); Dr. J. T. Dunn, D.Sc., F.I.C. (President of the Society of Chemical Industry); Mr. J. F. Blackshaw, O.B.E. (Dairy Commissioner, Ministry of Agriculture); Mr. James Stenhouse, A.C.G.I. (President of the Institute of Brewing); Dr. C. H. Hampshire, M.B., B.S., M.R.C.S., L.R.C.P., F.I.C. (Chairman of the Pharmaceutical Conference); Mr. J. Egerton Quested, J.P.; Mr. R. B. Pilcher, O.B.E. (Registrar of the Institute of Chemistry); and Mr. R. A. Beck.

After the toasts of His Majesty the King and the Members of the Royal Family had been honoured, the President proposed the health of the Houses of Parliament. Mr. Arnaud pointed out that Public Analysts owed their very existence to Parliament, for they were a direct outcome of the Food and Drugs Acts of 1860 and 1872, a large proportion of the regulations of which was incorporated in the 1928 Act. The Report of the Departmental Committee which was enquiring into the question of food standards was awaited with interest. Unquestionably, further legislation was required to bring our food laws into unison with those of the Dominions and European countries.

LORD CORNWALLIS responded for the House of Lords, and SIR ISIDORE SALMON, M.P., for the House of Commons. Sir Isidore said that it was now recognised that industries connected with the manufacture of foodstuffs were anxious to have them pure.

SIR WILLIAM J. POPE proposed the toast of "Success to the Society." He deplored the fact that students were doing less quantitative analytical work at the present day than in his young days, since such work involved training in scientific methods. He envisaged the time when the Public Analyst would be called upon to undertake the accurate chemical determination of vitamins. At present, these determinations were made by physiologists.

The PRESIDENT, replying to the toast, referred to the steady increase of the Society in numbers and in influence, and laid stress upon the fact that the Society's journal, THE ANALYST, had won for itself an international scientific reputation. Mr. Arnaud then proposed the health of Dr. and Mrs. Bernard Dyer. He said that Dr. Dyer had been associated with the Society from its inception, 60 years ago, had been its President in 1897, and had contributed largely to its growth and influence. Dr. DYER thanked the Society for the toast.

Dr. G. W. MONIER-WILLIAMS, in proposing the health of Kindred Societies, indicated how closely many of them were linked with the Society of Public Analysts.

Dr. CHARLES PORTER, in his reply to the toast, observed that the members of his Society (the Society of Medical Officers of Health) and of the Society of Public Analysts had together done more to benefit public health in this country than any other group of persons.

Dr. L. H. LAMPITT proposed the health of the Guests. In the course of his speech he referred to the recent appointment of Miss Muriel Roberts—the first woman to become a Public Analyst in England.

SIR ROBERT ROBERTSON, the Government Chemist, replying for the Guests, referred to the cordial relations existing between the Society and his Department, and to the fact that his staff made frequent use of THE ANALYST for the publication of analytical communications.

Mr. J. F. BLACKSHAW, Dairy Commissioner, Ministry of Agriculture, who also replied for the Guests, spoke appreciatively of the friendly relations existing between his Department and the Society.

Annual Report of Council

March, 1934

THE Roll of the Society stands at 702, a slight increase over the membership of last year.

The Society has sustained during the current year very serious losses of old and valued members, many of whom have been untiring in their energies to promote the prosperity of the Society. These include:

Edward Theodore Brewis
John Joseph Bryant
Ernest Griffiths-Jones
John Haworth
Thomas James Hutchinson
Alfred Edward Johnson
William Marshall
William Partridge
John David Roberts
George Tate
John Millar Thomson
Walter Peter Whitley
James Wood

J. Millar Thomson, at one time Professor of Chemistry at King's College, was an honorary member of the Society. He will be remembered by many who, as students at King's College, studied chemistry under him.

Brewis, 19 years a member, was mainly known for his activities on the Standing Committee, and in that capacity rendered valuable services to the Society. He had been a Member of Council and was a familiar figure at meetings.

Johnson and Wood, members for 10 and 15 years respectively, had both served on the Council, and the Council is grateful for their services.

Tate and Whitley had been members for 19 and 8 years respectively. Although not often seen at meetings they were both distinguished in their particular spheres of activity.

Partridge, during his 30 years of membership, had been a Vice-President and Member of Council. Although by nature somewhat shy and retiring, he was a regular attendant and was indefatigable in his endeavour to promote the welfare of the Society, particularly on the Publication Committee and as a member of the Standing Committee.

Hutchinson and Marshall were both very old members of some 40 years' standing, and the Council regrets their passing.

Bryant and Griffiths-Jones joined the Society in 1924, and Roberts, although a comparatively recent recruit, took a keen interest in the Society's affairs, and was our representative on the Empire Marketing Board's Dairy Research Sub-Committee.

Haworth, a member since 1919, was well known as an authority on the examination of water and sewage.

During the year seven meetings of the Society have been held, and the following papers have been communicated:

"Notes on the Iron and Copper in Liver and Liver Extracts." By H. G. Rees, B.Sc., A.R.C.S., A.I.C.
"The Determination of the Freezing-point of Milk." By G. W. Monier-Williams, O.B.E., M.C., M.A., Ph.D., F.I.C.
"An Investigation of Solanine Poisoning." By S. G. Willimott, Ph.D., B.Sc.
"The Examination of Leather for the Presence of Extractable Chromium Compounds." By F. E. Humphreys, Ph.D., A.R.C.S., A.I.C., and H. Phillips, D.Sc., F.I.C.
"Use of the Phytosteryl Acetate Test in the Routine Examination of Butter Fats." By H. Hawley, M.Sc., F.I.C.
"Barium as a Normal Constituent of Brazil Nuts." By W. M. Seaber, B.Sc., F.I.C.
"The Occurrence and Origin of Lead in Canned Sardines." By L. H. Lampitt, D.Sc., F.I.C., and H. S. Rooke, M.Sc., F.I.C.
"The Chemical Examination of Furs in Relation to Dermatitis." Parts II, III and IV. By H. E. Cox, M.Sc., Ph.D., F.I.C.
"The Investigation of Japanese Beeswax." III. By H. Ikuta.
"A Specific Gravity Apparatus." By C. H. Cribb, B.Sc., F.I.C. Demonstrated by T. McLachlan, F.I.C.
"The Use of the Air-Damped Balance for the Determination of Total Solids in Milk." By Capt. John Golding, D.S.O., F.I.C.
"A Rapid Method of Determining Minute Quantities of Nitrites." By G. G. Rao and K. M. Pandalai.
*"The Analysis of Fruit and Fruit Products." By E. B. Hughes, M.Sc., F.I.C., and A. E. Maunsell, B.Sc.
*"The Examination of Fruits and Jams by Lead Precipitation." By C. L. Hinton, F.I.C.
*"Equalisation of Temperature in Electric Ovens." By F. G. H. Tate, F.I.C.

The North of England Section held five meetings, at which the following papers were read:

"Ancient Egyptian Materials and Industries about 1350 B.C." By A. Lucas, O.B.E., F.I.C.
"Foreign Starch in Arrowroot." By P. H. Jones, F.I.C.
"A Note on Pearl Barley." By P. H. Jones, F.I.C.
"The Examination of 1000 Milks by the Hortvet Freezing-point Process." By J. R. Stubbs, M.Sc., F.I.C., and G. D. Elsdon, B.Sc., F.I.C.
"Note on Nitrates Test in Milk." By W. F. Alvidge, B.Sc., F.I.C.
"The Effect of Certain Salts on Fermentation in Dough." By R. H. Callow, M.Sc., A.I.C.

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* Read at the Joint Meeting with the Food Group of the Society of Chemical Industry on February 7th, 1934.

"Note on Freezing-point Determination—Hortvet's Method." By E. V. Jones, F.I.C.

"Some New Applications of the Elaidin Reaction in the Examination of Fatty Oils." By Prof. T. P. Hilditch, D.Sc., F.I.C.

Of the Society's Meetings, one, namely the November meeting, may be mentioned. A discussion on the Chemical (as distinct from Physiological) Tests for Vitamins, opened by Mr. A. L. Bacharach, who was followed by many distinguished speakers, made an interesting and valuable contribution. In recent years it has been the policy of the Council to hold these discussions, and they are tending to increase in number. Without in any way desiring to limit the time available at Ordinary Meetings for the readers of papers, the Council feel that discussions on general analytical problems tend to promote interest and add generally to the usefulness of the Society's Ordinary Meetings.

THE ANALYST.—Although THE ANALYST for 1933 contains a somewhat smaller number of pages than in the previous year (789 as compared with 810) this does not mean any curtailment of the activities of the Journal, but is due to the papers being more concise than in former years. The total number of papers (including those not read before the Society) was 48, and there were also 49 Notes. The catholicity of the interests of the Society is shown by the fact that, of the 48 papers, 18 were concerned with the analysis of food and drugs, 13 with inorganic analysis, 7 with toxicological and forensic work, 5 with organic analysis, 2 with archaeological research, and 1 with micro-analysis. A similar diversity of interest is to be found in the Notes.

Of the papers published, three were the outcome of work under the Society's Analytical Investigation Scheme. Mr. T. H. Pope's valuable compilations of the Bibliography on Heavy Metals in Food and Biological Material have been continued during the year and have since been completed. They have attracted wide attention, and are now being reprinted together as a brochure.

Official and Public Analysts at home and abroad have, as in former years, sent copies of their Annual Reports to the Editor, and these have provided the material for numerous notes of value to analysts. Several reports on legal cases have also been forwarded by the chemists concerned in them, and whenever these have involved certain points of special legal or scientific interest they have been abstracted in a form convenient for reference.

As in the past, papers of direct or indirect analytical interest published in other journals have been abstracted and submitted to the criticism of the Publication Committee, to insure that, so far as is possible, the subject-matter is novel, and that sufficient working details are given to enable the methods described to be tried. Reviews have continued to be a prominent feature of the journal.

TREASURER'S REPORT.—The Honorary Treasurer reports that the accounts for 1933 show that the Society has maintained its usual satisfactory financial position, the income fully meeting the expenditure involved during the year.

STANDING COMMITTEE ON UNIFORMITY OF ANALYTICAL METHODS.—The following reports have been published:

Report No. 1 (Determination of Unsaponifiable Matter in Oils and Fats) of the Sub-Committee on Determination of Unsaponifiable Matter in Oils and Fats and of Unsaponified Fat in Soaps has been received and adopted by the Council, and published in THE ANALYST (1933, 58, 203). This Sub-Committee has been re-constituted, with Mr. L. V. Cocks as Chairman, and Mr. N. Evers as Honorary Secretary, and Dr. H. E. Cox and Mr. P. L. Bean as new members, Professor Hilditch having resigned.

Report No. 11 of the Essential Oil Sub-Committee has similarly been passed for publication, and it appeared in the February number of THE ANALYST. The work of these and other Sub-Committees is proceeding, but there are no further reports ready for publication.

The Standing Committee has lost two of its members, E. T. Brewis and W. Partridge, by death; the Milk Products Sub-Committee has also suffered loss by the death of J. D. Roberts.

Mr. A. More has been elected a member of the Standing Committee.

ARTICLES OF ASSOCIATION.—The Council asks that three alterations in the Articles of Association be approved at the Annual General Meeting:—(1) To add, in accordance with the demand of the Board of Trade, the words "if and while unpaid" to the Article relating to the *ex-officio* election of the Chairman and Hon. Secretary of the North of England Section to the Council. (2) That members, who have paid 40 annual subscriptions shall *ipso facto* become life-members of the Society, with full privileges, without payment of further subscription. (3) That the entrance fee of members nominated by the North of England Section be waived.

NORTH OF ENGLAND SECTION.—The Section reports as follows: Five meetings have been held during the past year. A Sub-Committee sat in February and, after discussion, drew up recommendations for obtaining uniformity of design of apparatus and method of procedure for determining the freezing-point of milk.

In April a symposium, at which there was a large attendance, was held on "The Freezing-Point of Milk as a means of Detecting Added Water." After discussion, resolutions were passed for submission to the Council; these were duly sent in and the Council issued a recommendation that, for the present, the Hortvet apparatus and method of procedure should be adopted (ANALYST, 1933, 58, 318).

A very successful Summer Meeting was held in June at Llandudno. It was well attended and thoroughly enjoyed. We were favoured with the presence, among others, of Dr. and Mrs. Bernard Dyer. A paper read by Mr. A. Lucas was much appreciated; it was afterwards published in THE ANALYST (1933, 58, 654).

The attendance at meetings has been higher than in any previous year. Eighteen new members have been enrolled. The Section has lost by death two members: James Wood, who served on the Committee and the Council, and William Marshall, who held the office of Auditor from the time the Section was inaugurated (see p. 214).

The Secretary wishes to express his sincere thanks to the Chairman, Mr. John Evans, and all members of the Committee, who have one and all contributed to make every meeting a thorough success.

ANALYTICAL INVESTIGATION SCHEME OF THE SOCIETY.—During the past year two grants were made from the fund. Three researches were completed, and six problems are still under investigation. The Council wishes to call the attention of younger members of the Society to the work that is being carried out under the Scheme, and to assure them that they may rely upon the assistance of individual Members of the Council in overcoming difficulties that may be encountered in the course of an investigation.

BRITISH STANDARDS INSTITUTION.—Conversations have taken place between representatives of the Institution and of the Society directed towards the possibility of establishing co-operation in the matter of standard analytical methods.

PUBLIC ANALYSTS' COMMITTEE.—Several meetings of this Committee have been held during the year, the chief work being carried out at the request of the Malt Vinegar Brewers' Federation. A series of conferences has been held with that body in order to draw up definitions of Vinegar. These definitions are now completed, and have been approved by the Council and the Federation. It is hoped soon to publish these in THE ANALYST, but the Council feels that until the findings of the Departmental Committee on Food Law are published it would be premature for these definitions to be set out in THE ANALYST.

DEPARTMENTAL COMMITTEE ON FOOD LAW.—This Committee, which was to have met some two years ago, and whose activities were temporarily postponed for reasons of economy, commenced to hear evidence last September. The Society submitted to the Committee a memorandum which they had drawn up in 1931, together with a letter and appendix containing certain important material which was not available at the time the original memorandum was compiled. The Council nominated the President, Mr. Hinks and Dr. Dunn to give evidence before this Committee, and they were heard early in October.

INDUSTRIAL CHEMISTRY CONGRESS AT LILLE.—At this Congress, which was held in September, the Society was represented by Dr. Lampitt, and the Council thanks him for acting as its delegate.

EMPIRE MARKETING BOARD.—The Council notes with regret the dissolution of the Board, which must result in a certain amount of delay in connection with work in the progress of which the Society is particularly interested.

CENTRAL COUNCIL FOR RIVERS PROTECTION.—This Council wrote to the Society, asking that we federate, and that a member be nominated to serve upon this important body. The President, Mr. Arnaud, has consented to serve.

The Biennial Dinner, which the Council has decided to hold this year, marks the 60th anniversary of the foundation of the Society. Although the first general meeting was not held until February 5th, 1875, it is noteworthy that a meeting was held in August, 1874, at which it was agreed that a Society be formed.

The Council extends its hearty congratulations to its Past-President, Dr. J. T. Dunn, on his election as President of the Society of Chemical Industry, and on the fact that he has completed fifty years of membership of the Chemical Society.

The Council again desires to record its thanks to those members who have acted as representatives on various Committees, Federations and Institutions and other organisations during the year, and deeply appreciates the services they have given.

In conclusion, the Council, whilst regretting that the time has come for Mr. Arnaud to vacate the Presidential chair, welcomes the new President, Mr. John Evans, and looks forward to a period of continued prosperity under his guidance.

(*Signed*) F. W. F. ARNAUD, *President.*
G. ROCHE LYNCH, *Honorary Secretary.*

Annual Address of the President

(Mr. F. W. F. ARNAUD, F.I.C.)

(Delivered at the Annual General Meeting, held on March 2, 1934)

LADIES AND GENTLEMEN,

It is gratifying to be able again to report that the Society has had a successful year, successful because we record an increase in the number of members, our financial position remains very satisfactory, and our Ordinary Meetings have been well attended. It is not surprising that our Ordinary Meetings have been attractive when the importance of the papers communicated is considered.

Our losses have been unduly heavy, and we mourn the loss of several valued members. The memory of Professor J. Millar Thomson, one of our honorary members, will live for all time with those of us who were privileged to work under him at King's College. His invariable good humour alone was sufficient to endear him to all his students. The list of deaths includes the names of James Wood, E. T. Brewis, A. E. Johnson and William Partridge, who were past or present Members of the Council, and we shall ever have grateful memories of these colleagues.

The Standing Committee on the Uniformity of Analytical Methods and its Sub-Committees have issued further reports during the past year, and your Council has passed a resolution of thanks and appreciation to the Chairman and members of all the Committees for the labours entailed in the production of the reports. The Standing Committee, through your Council, has already supplied information concerning standard processes, etc., to the British Standards Institution, and it is possible that some working arrangement will be made so that the Society will in the future supply methods of analysis when requested by the British Standards Institution.

During July last the Minister of Health and the Secretary of State for Scotland directed that the work of the "Food Law" Committee appointed in 1931, under the Chairmanship of Sir Frederick J. Willis, should be resumed, the terms of reference being "To consider whether it is desirable that the law relating to the composition and description of articles of food should be altered so as to enable definitions or standards to be prescribed, or declarations of composition to be required, for articles of food other than liquid milk; and, if so, to recommend what alterations of the law are required." A Memorandum agreed upon by your Council was presented to the Committee by representatives of the Society. The Committee has not yet completed its task, and evidence is still being heard from various interested organisations.

At the request of the Malt Vinegar Brewers' Federation, definitions of malt vinegar and vinegar were drawn up by one of your Committees, and these were agreed to both by your Council and by the Federation. These definitions may prove extremely useful in the future, and they at least have the merit of being definitions agreed to by the trade and by the chemist.

The Institute of Chemistry has on many occasions very generously placed accommodation at the disposal of the Society for meetings of its Committees, and I express the gratitude of the Society to the President and Council of the Institute for the practical help they are ever willing to extend to us.

This evening I intend to devote my remarks to some aspects of the agricultural industry, and particularly to those to which agricultural chemistry has some relationship and application. Further, my remarks are largely limited to matters within my experience.

Unquestionably everyone appreciates that modern farming involves the application of many scientific principles, some of which are well, but many only very imperfectly, understood. So many different factors have to be taken into account that the solution of some agricultural problems becomes almost impossible, for many of the factors represent unknown quantities. Soil fertility is, perhaps, one.

Examination of Soil.—Having mentioned soil, I will deal with this subject first, as a farmer often seeks advice about what has been termed his raw material.

Frequently a soil is submitted for examination because the farmer wishes to ascertain which fertilisers to apply to the soil, and the most suitable form in which to use them. In brief, he requires to know what quantities of nitrogen, phosphates, potash and lime should be added to his soil to give him the best return. The position with regard to nitrogen is anything but satisfactory, since, even though an examination of a soil may show it to contain a high percentage of nitrogen, yet it can generally be predicted with confidence that the soil will give an increased yield of crops on the application of a soluble nitrogenous salt. Various basic quantities of nitrogen have been suggested from time to time, but the fact remains that soil fertility must for ever be bound up with weather conditions, drainage, position and other considerations. The crop to be grown or manured must also be carefully considered, because the requirements of plants differ, and there may be but little response to anything more than a minimum dressing. Often some indication of probable soil-fertility and response to nitrogen dressings can be obtained by comparing the total nitrogen-content with that present in soil of similar formation and character occurring elsewhere in the neighbourhood, and whose performance and reaction to nitrogen dressings are known. Often the desired information is not easy to obtain. To determine the soil character, a mechanical analysis usually gives the most useful information. The total nitrogen in a soil is determined by means of the Kjeldahl–Gunning process or a similar one, about 10 grms. of the air-dried soil being used. Some information as to availability may be obtained by determining the nitrogen as ammonia and the nitrogen as nitrate in the fresh soil. The nitrogen as nitrate in a cultivated soil is usually higher than in an uncultivated soil, but active plant growth may result in a cultivated soil having but a low nitric nitrogen content.

The small influence of repeated applications of nitrogenous manures on soil composition is well illustrated by some experiments in America. A few years ago the New York Agricultural Experimental Station published the chemical analyses of eight soils which, 17 years before, had been sampled and analysed.

During the intervening years these soils had been variously cropped and manured. All the soils but one had received annual dressings of nitrogen in differing amounts and in differing forms, farmyard manure, dried blood or nitrate of soda having been used. The final analyses of these soils showed that, for practical purposes, the nitrogen in all of the soils had remained constant, despite cropping and treatment. From this it must not be understood that no changes in soil composition, owing either to plant growth or the addition of fertilisers, can be detected, because in some instances changes of great importance have been recorded; there is, for example, the increase in soil-nitrogen in uncultivated land, and also in land under grass and clover, even when the crop is mown. How easily an unwarranted conclusion could be based on the total soil-nitrogen alone is exemplified by a consideration of the Folkestone beds. These beds usually produce little but scrub and heather, and yet often contain about 0·2 per cent. of nitrogen, whereas a good strong wheat soil may contain considerably less.

The difficulty in suggesting a useful addition of nitrogen to a soil from the result of a nitrogen determination will be readily appreciated when the weight of top soil is considered in relation to the percentage effect of a dressing of nitrogen. Assuming a top soil to weigh 1000 tons to the acre, and to contain 0·2 per cent. of nitrogen, it would be necessary, in order to increase the nitrogen to 0·3 per cent., to add at least 1 ton of nitrogen per acre, and this would be equivalent to about 200 tons of farmyard manure.

Determinations of the total phosphates and potash are usually made by treating the air-dried soil with boiling hydrochloric acid, diluting with water and filtering. Obviously, results obtained on such a solution do not really indicate the total phosphates or potash in the soil, but only what is rendered soluble under the conditions of the test.

Of more importance, in judging the fertility of a soil, is knowledge of the amounts of phosphates and potash that are readily available for plant growth. Various solutions have been suggested, and tried, to improve the method devised by Dyer forty years ago, but opinion strongly supports the view that Dyer's original process gives good, and probably the most reliable, information as to the ease with which phosphates or potash in the soil may be taken up by plants. The "available" phosphates are determined by acting on the air-dried soil with a 1 per cent. solution of citric acid either for 7 days or for 24 hours if continuously shaken. Though the method is empirical, the utility of the results is unquestionable. The citric acid solution does not dissolve all the phosphoric acid or potash available for plant-growth, but the amounts dissolved form a basis for comparison with those dissolved from similar soils of known fertility and, therefore, they may indicate manurial requirements. Further, the results indicate when the amounts of available phosphates or potash are so low as barely to support plant life. In America, instead of 1 per cent. citric acid solution, the use of $N/5$ hydrochloric acid or $N/5$ nitric acid has been advocated, and other chemists have favoured the use of a saturated solution of carbon dioxide.

Attention has recently been directed to the ratio of citric-soluble phosphates to "exchangeable" potash. From some published results it would appear useful to pursue this method further as a means of determining soil condition and requirements. The exchangeable soil bases are determined by liberating them from a soil by means of a neutral salt such as ammonium chloride. Sodium chloride should be used if exchangeable lime is required.

From what has already been said it must be apparent that the mere chemical analysis of a soil does not usually yield information of great practical value, but when the results can be compared with those of soils of known performance, useful conclusions may sometimes be drawn. But even the interpretation of field trials is not an easy matter, and trials should extend over several years at least. In Kent, as in some other counties, a soil survey has been made, and the results have been published, and this survey is of very great utility. Rather more than 20 years ago Hall and Russell published a very comprehensive series of analyses of Kent, Surrey and Sussex soils, and it is to be regretted that this useful volume has long been out of print.

In Kent, information is normally required on soils used for special crops, such as hops and various fruits.

Though difficulty usually exists in the minds of those qualified to advise the farmer of the possibilities of his soil, etc., from a chemical analysis, firms occasionally advertise that they will undertake a soil analysis for a few shillings, and then advise the farmer as to the necessary manures to apply, together with the quantities per acre. One of these reports made on a sample of arable soil was brought to my notice, and may be quoted as an example. It stated that the soil was "somewhat on the poor side in general character," and it advocated, amongst other things, dressings of sewage sludge (which was categorised as a highly organic manure) and 1½ cwts. of sulphate of iron per acre. As the soil in question already contained nearly 3 per cent. of iron (ferric oxide), it was difficult, indeed, to imagine by what reasoning further small quantities of iron were demanded. The suggestion that sewage sludge was a "highly organic manure" was also somewhat strange, as a good dry sewage sludge contains only about 20 per cent. of organic matter.

Iron is often applied to lawns, as it promotes chlorophyll production and, therefore, a green grass. Sulphate of iron has an adverse effect upon some weeds, and particularly on moss, and it is a common constituent, together with sulphate of ammonia, of lawn sand.

Only a very brief reference need be made to some of the other methods directed to indicate the manurial requirements of soils, because I have had no experience with them. For instance, test plants have been used which have an ash containing a known ratio of phosphoric acid to potash. On growing these plants in a soil deficient in phosphoric acid or potash a disturbance of this ratio occurs in the plant ash. Another method involves the use of a specified fungus, which is seeded in a suspension of the soil to which has been added the ingredients necessary to promote the growth of the fungus, but not including the element for which the soil is being tested. After a specified time the mycelium which has developed on the surface is removed, dried and weighed. A principle which has been applied for the cultivation of the sugar cane involves the determination of phosphoric acid and potash in the juice, and minimum limits for both phosphoric acid and potash have been suggested. If either limit is not exceeded, manuring with phosphates or potash is required.

It is of interest to note that at the East Malling Research Station a method has been devised for introducing solutions direct into trees. Experiments have demonstrated that the introduction of potassium nitrate results in a marked increase in vigour, and the research is being continued in connection both with fertilisers and with substances known to have an injurious effect on various plant diseases. Moreover, extracts from varieties of trees which are never infected with certain parasites have been injected into trees that are susceptible to infection, to note whether immunity from attack can be conferred.

Soil classification normally means the classification of soils according to their texture, a soil-texture being dependent on the size of the particles of which it is composed. To determine the texture, a mechanical analysis of a soil is made, the differentiation of the particles of various sizes being effected, first by means of sieves, and then by sedimentation from water. By these means soils can be graded into fractions known as gravel, fine gravel, coarse sand, fine sand, silt, fine silt and clay. Unfortunately, from time to time, the conditions of experiment have been altered, with the result that the soil fractions obtained by the varying processes are by no means identical. Finality may have been reached, however, since the Imperial Bureau of Soil Science has recently issued a report on the dispersion of soils in mechanical analysis, and in it are given details of a recommended procedure. It is to be hoped that the recommendations will be adopted throughout the Empire, so that there will be conformity to a uniform procedure. Many workers in localities where a soil survey has been published will, however, cling to their old methods, because these methods yield results which can be directly compared with those previously published. Mechanical analysis enables a soil to be classified, and thereby a comparison to be made with similar soils, and so classification may lead to a soil-response to fertilisers being foretold. Mechanical analysis also yields information on soil texture, and thus renders apparent the possibilities of cultivation, the water-holding power and other properties of the soil.

In many instances the whole of the soil down to the unweathered material is of importance in crop production. Each soil layer may have a material influence on the movement of water either in a downward or upward direction and, therefore, the mechanical analysis of the top nine inches of soil may give quite a false value to the real water-holding capacity of a soil, particularly where the natural subsoil water level is high. Much attention has recently been given to soil horizons (depth of soil layers), and the differences in fertility of similar soils in a neighbourhood have been thereby explained. Of course, the difference in the performances of similar soils may be due merely to differences in the depth of top soil.

Some success has attended recent endeavours to forecast soil suitability for various crops (particularly fruit) by means of the identification of soil variety and condition in the field. This method involves the classification of soils in "soil series," these being sub-divided into "soil types." The system is dependent on the observer being able to recognise, by inspection, its geological origin and its mode of production. Then its position is noted, whether on a hill, hill-side or valley, and finally its drainage, profile and texture. As a result of this examination, an expert may, with some assurance, express an opinion whether a particular crop may be grown with success; but the ideal manurial treatment is a problem still awaiting solution.

No laboratory examination of a soil could be considered complete unless it included the determination of lime, and also indicated whether the soil contained sufficient lime to ensure that it did not possess an acid reaction. The restrictions to the deductions that can be drawn from an ordinary soil analysis do not apply to the examination of a soil for lime. The effect of lime on a soil is not only chemical and mechanical, but also biological, as only in its presence can beneficial organisms, such as the nitrifying organisms, flourish. Though there are agricultural plants which will grow in sour soils, these are usually of small economic importance. Some crops are more tolerant of soil sourness or acidity than others; for instance, potatoes and oats may grow well in a sour soil, but clover and barley show less tolerance. A considerable proportion of the superficial area of Kent is covered with chalk, or has chalk immediately below the surface, yet lime-deficient soils are constantly being found, even when the soils are on chalk formations. Soils on the Kentish ragstone, and the result of weathered ragstone, are often seriously lime-deficient, although ragstone contains from 70 to 75 per cent. of carbonate of lime. The figure of 800 lbs. per acre of lime has been suggested as an annual lime loss per acre. Often the need of lime in a soil can be foretold by the absence of worm casts and the presence of certain weeds. Weeds on a sour soil may flourish, not only on account of their ability to grow almost in an absence of lime, but also on account of the agricultural plant being weak and attenuated and unable to smother the weed crop. Various tests have been devised to test soil sourness, including the determination of the p_H value. Often the farmer is recommended to test his soil by adding hydrochloric acid, when an effervescence indicates the presence of calcium carbonate. Aqueous extracts of sour soils have iron in solution; hence, a test frequently applied is that of adding to the dried soil a 10 per cent. solution of sodium salicylate or a saturated solution of thiocyanate in alcohol, when sourness is indicated by a red colour of the solution. Soluble aluminium is also associated with soil sourness, and the aluminium soluble in semi-normal acetic acid bears some relation to lime requirement. The total calcium carbonate in a soil calculated from a carbon dioxide determination does not always give a reliable indication of the probable response of a soil to lime. Russell has recorded instances of soils containing only 0·02 and 0·03 per cent. of calcium carbonate which did not benefit from lime applications, the reason being that the soils were supplied with subsoil waters rich in lime. The total lime soluble in hydrochloric acid includes lime combined as salts as well as lime as carbonate, and it is the latter form of lime which is so important, so far as the free working of the soil and its freedom from acidity are concerned. The lime-magnesia ratio is important, because when magnesia is present in excess of lime, land may respond to lime dressings, even though it contains appreciable quantities of carbonate of lime. On the other hand, Voelcker has shown that, under certain conditions, yields of wheat can be increased by the addition of magnesia. Chlorophyll contains magnesium. In general, the need for lime becomes greater as the amount of clay increases, because of the need of flocculation. The lime-requirement of a soil to correct acidity may be ascertained with some degree of accuracy by the process devised by Hutchinson and MacClennan, and this process we carry out on all soils (ANALYST, 1914, 39, 450). However, dressings of lime to-day are largely curtailed by the financial capacity of the farmer to purchase. When a lime-dressing to a sour soil is advised, consideration must be given to the possible amount of organic nitrogen which may have accumulated, because this nitrogen will be largely rendered available. For instance, lime applied to a sour soil before a corn crop may result in a length of straw which will cause the corn to lie. As lime encourages clover, applications to lawns should not ordinarily be made; indeed, in such a case acid manures, such as sulphate of ammonia, tend not only to keep down weeds, but also to promote the growth of the grasses required.

Among some twenty elements, other than those already discussed, invariably present in plants, are sulphur, copper, fluorine, iodine, chlorine, zinc, cobalt, and nickel. Exact information does not exist as to the importance of all of these elements in the plant, and whether certain of them are merely present because they happen to exist in the soil water and become absorbed. Spectrographic methods for the determination of ash constituents are being employed at East Malling Research Station. I have only had occasion to enquire into the presence of two of the above elements in soils, namely, sulphur and copper.

Gypsum applied to soil has been said to increase both the soluble potash and phosphoric acid, but, within my knowledge, little gypsum is now used as a fertiliser. It was advocated at one time as a source of sulphur, but most soils contain ample quantities of sulphur in the form of sulphate from fertiliser residues, such as sulphate of ammonia and superphosphate. Extractions with hydrochloric acid of six different arable soils showed them to contain the following amounts of sulphate:—0·076, 0·074, 0·130, 0·167, 0·126, and 0·086 per cent. Sulphur, itself, has been used as a soil-dressing to provide sulphur, to render plant foods more soluble, and as a preventive of some plant diseases, *e.g.* potato scab.

Copper is often to be found in very appreciable traces in plants and plant-products, but the quantity varies considerably. Determinations made during recent years showed Kent products to contain, for instance: Hay, 1/20, 1/15; clover (dry), 1/10; wheat straw, 1/14; nettles (dry), 1/36; grass, 1/36; thistles, 0; linseed cake, 1/7-1/5; hops, dry (growth 1925–1926), 1/70–1/4; malt, 1/2, 1/2. These results are expressed in grains of copper per pound. Examinations of four samples of beer from different breweries in 1928 revealed copper in amounts varying from 1/15 to 1/10 grain per gallon. Copper is a constituent of various sprays; for instance, it is used on fruit trees for scab, potatoes for blight, and on hops for downy mildew. The sprayed leaves contain considerable amounts of copper, much of which may not be washed from the leaves by rainfall. Summer-sprayed autumn-fallen apple leaves I have found to contain as much as 2·5 grains of copper per pound. The processes used in these determinations were published in THE ANALYST (1926, **51**, 328; 1929, **54**, 650; 1932, **57**, 495). We have found the quinosol process excellent when not less than 5 grms. of material can be taken, and at least 1 grain of copper per pound is present, but with smaller quantities the di-ethyldithiocarbamate process is used. Soils invariably contain some copper; we have determined the following amounts:

Poor grass land	1/14 grain per pound.
Under bush fruit	1/9
Fruit land	1/3
Hop garden	1/14
Grass land	1/10
Apple orchard (arable) ..	1/7

FERTILISERS AND FEEDING STUFFS.—Of fertilisers and feeding stuffs, I have examined considerably more than 15,000 samples during the last twenty years, and the processes mainly used have been those contained in the Regulations issued under the Fertilisers and Feeding Stuffs Acts. These official processes have been well tested throughout the country, and, although they were adopted without any prolonged investigation in different laboratories, they have given extremely satisfactory results. Many of the samples submitted to me have also been submitted to other laboratories, and a comparison of the results shows excellent agreement.

The Kent agriculturist may be said to be noted for his use of rough fertilisers, for almost every form of waste is utilised by him. Foremost among these manures must be placed shoddy, the annual consumption of which amounts to several thousand tons. Shoddy is purchased on a valuation based on its nitrogen-content; a sale may be effected on a nitrogen warranty or at a price per unit of nitrogen. Very little shoddy is now sold without any kind of warranty or stipulation and, therefore, the days when vendors found it profitable to water it before sale are gone. Of necessity, shoddy must vary considerably in quality, as wool and silk refuse contain about 13·5 per cent. of nitrogen, whereas cotton and many fibres used in the textile industries contain less than 1 per cent. However, the composition of truck loads from factories is remarkably uniform, and there has been much exaggeration concerning the difficulties of sampling and the analysis to obtain the true composition of shoddy. We have, on several occasions, had medium-grade shoddy re-sampled, and in every case have obtained extremely concordant results on the duplicate samples. These shoddies have included mixtures of wool with vegetable fibre, and also mixtures in which the loading material has been sandy matter. Truck after truck from a factory may show but little variation, and the accuracy with which sellers determine the nitrogen-content of loads, without chemical analysis, is remarkable. Many different types of "shoddy" are sold; for instance, shearings (wool clippings), carpet waste, wool combings or grey shoddy (rough wool combings often containing many weed seeds), daggings (soiled raw fleece wool), wool dust, etc. There are no stated grades of shoddy, but they are usually classified according to the amount of nitrogen they contain. A high-grade shoddy contains more than 12 per cent. of ammonia, medium-grade between 5 and 12 per cent., and low-grade less than 5 per cent. of ammonia. When a shoddy is sold with a warranty, the warranty invariably states the nitrogen in terms of ammonia, there being no compulsion to refer otherwise to its composition. It is quite possible to adulterate shoddy with sulphate of ammonia, and I have found low-grade shoddy to have been enriched through its addition. Of recent years the unit value of nitrogen in sulphate of ammonia has been below that of nitrogen in shoddy. The value of the nitrogen in shoddy delivered at a farm station varies from year to year; at the moment it is about 8s. 6d. per unit. Other wastes purchased as a source of nitrogen are rabbit fur, rabbit flick (fur only), rabbit fur waste (contains ears and legs), skin waste (sometimes called fleshings), feathers, feather quills, wings of birds, hairs (pig, calf, goat), silk waste, silk cocoon dust, felt waste (including torn-up waste from gun cartridge wads), ivory dust, casein waste, seal fleshings, chamois dust, etc. All these wastes are of variable composition owing to the possibility of admixture with non-nitrogenous matter, particularly sand or soil. A rabbit fur waste may consist of fur only, or it may contain a large proportion of legs; in the former case the waste will have a high nitrogen-content (about 13 per cent.), whereas the latter will probably not have more than 8 per cent., and it will have a bad spreading value on account of its dense character. The condition of all waste manures is important, because an offered consignment may consist of material in large pieces. For instance, rabbit fur waste may be composed of large pieces of fur and skin or of small clippings, and it must be obvious that the small clippings are not only easier to apply, but also that they can be applied to land more evenly and will possess a greater covering power.

Several materials are used within our county that are but very rarely used in counties with less sea border, such as, for instance, mussels, star-fish, limpets, sprats, and seaweed. These may be termed waste products of sea-fishing and of the sea. Mussels, as they are dredged, contain about 1 per cent. of nitrogen, and star-fish ("five-fingers") double that amount. Recently, attempts have been made to dry limpets and to grind them thoroughly; the dried product contains about 0·5 per cent. of nitrogen and somewhat more than 90 per cent. of carbonate of lime. These shell-fish have only a very small phosphate- and potash-content.

I do not propose to mention the many well-known nitrogenous fertilisers freely sold throughout the country, for their uses and values are well known. This also applies to fertilisers containing phosphates or potash.

Sometimes difficulty is experienced in suggesting the manurial value of nitrogenous manures, and it occasionally happens that there are no published field trials that afford help.

Various methods have been devised for testing the quality of insoluble organic nitrogen, and such methods have received considerable attention in America. One of these methods is contained in the Official Methods of Analysis of the Association of Official Agricultural Chemists. In the processes now recommended by the A.O.A.C. both the water-insoluble organic nitrogen soluble in neutral permanganate solution and the water-insoluble organic nitrogen soluble in alkaline permanganate solution are determined. Originally the method was used to determine the availability of organic nitrogen, but it is now accepted rather as a means of merely distinguishing between good and poor sources of nitrogen. But some of the materials which are accepted as good sources of nitrogen for the soil give poor results, so that results obtained by the processes must be interpreted with caution.

The two chief forms of lime used in farming are the oxide and carbonate. The former may be sold merely as burnt lime or slaked lime or partly slaked lime. In the case of the carbonate, not only is the amount of pure calcium carbonate important, but also its degree of fineness. According to published experiments, no benefit resulted during two years from an application of calcium carbonate, none of which passed the 100E sieve, and it has been advocated that all limestone or chalk should pass at least the 60-mesh sieve, as coarser particles are of little value. On the sale of ground limestone it is compulsory that a warranty be given of the amount that will pass a prescribed sieve. A slaked lime is often offered for sale, containing variable proportions of lime with upwards of 20 per cent. of water (combined), and the material finds some favour, because, being less dusty than ordinary lime, it is not so dangerous to the farm labourer who applies it to the land. We have found that limes offered to agriculturists vary so much in composition that an analysis is essential for their evaluation, and the material has rightly been included in the Schedules of the Fertilisers and Feeding Stuffs Act. Some experiments have demonstrated that calcium silicate is effective in reducing soil acidity, and that, for instance, even open-hearth fluor spar slags low in phosphates have a value for their lime. In some counties sea-shore sand contains sufficient calcium carbonate to render it a valuable source of lime, and farmers near such coasts have made use of these supplies.

The chemical examination of feeding stuffs is possibly of more importance than formerly, because owners now generally feed their livestock on scientific principles, and this demands a knowledge of the composition of the foodstuffs used. A dairy cow, for instance, will receive a "maintenance" ration, to cover ordinary daily wastage, and also a "production" ration to compensate for the material contained in her milk. Thus, not only is the kind of food important, but also its composition. A ration is usually stated in terms of starch equivalent and protein equivalent, the latter being a figure half-way between the digestible crude protein and the digestible true protein. In pig-feeding the nutritive or albuminoid ratio is of importance, as the supply of proteins is thereby regulated. The nutritive ratio may be obtained from the digestible oil, carbohydrates, fibre and protein. The amount of digestible oil, digestible proteins, etc., in a feeding stuff is obtained from the total oil and proteins by the use of factors which have been obtained from experiments on livestock.

An examination of a feeding stuff is not complete unless it includes the search for deleterious seeds and other substances. A feeding stuff may contain less than the warranted amount of oil or albuminoids, or it may contain an excess of sand or an excessive quantity of fibre owing to the presence of much husk or shell, but it is important also to ascertain that a food is reasonably safe to give to stock. An adventitious seed liable to occur in feeding stuffs is castor, and, despite the many precautions that are now taken to ensure its exclusion, it is still, from time to time, found in dangerous quantities. As the occurrence of castor in a food is always accidental, it follows that it is generally badly distributed, and, whilst one sample of a cake may contain appreciable quantities, another sample of the same cake may be castor-free. Quite recently I found in a sample of cake three or four almost whole castor beans, but a thorough search in the remainder of the cake failed to reveal a further quantity, and stock were fed on the cake without any resulting injury. Owing to the small quantity of castor that may adversely affect stock, and, perhaps, in particular, milking cows, and also its uneven distribution, it follows that the sample of cake examined must be large before castor can be certified to be absent. Samples up to one pound in weight may be examined, especially when suspicion attaches to a food.

Inorganic poisons are not frequently encountered in feeding stuffs, but lead or arsenic occasionally occurs.

The possibility of the presence of a cyanogenetic plant must be remembered when injury from a feeding stuff is alleged. For instance, several different beans contain appreciable quantities of a glucoside capable of producing hydrocyanic acid, and for this reason they are useless as food for animals. Linseed invariably gives rise to a quantity of hydrocyanic acid when it is allowed to stand in contact with water, and the possible effect of the hydrocyanic acid so produced has been a subject of some controversy. A few years ago the Government of Northern Ireland thought the matter of sufficient importance to issue a warning that cattle of all ages were liable to be poisoned by the incorrect use of linseed and linseed cake. They were, however, of opinion that no injury could follow the use of linseed if given in a dry state, whether whole or crushed, or after treatment with boiling water. Considerable danger, however, existed if linseed were steeped in warm or even cold water so that enzymic action could proceed, with the consequent production of hydrocyanic acid. During 1910, Lander made several experiments with linseed cake and also with hydrocyanic acid itself. He fed two sheep on cake, which yielded 0·025 per cent. of hydrocyanic acid, one of the sheep receiving one pound of cake for 36 consecutive days, and one for 10 days, during which it received a maximum of 5 pounds per day. No ill-effect resulted. A six-months heifer received 261 pounds of the cake in 67 days, with no adverse effect. Potassium cyanide, itself, was then administered to a heifer, 61·0 grains (HCN) being given in 10 days, the maximum dose being 15·0 grains (HCN), again with no obvious result. A 30-grain dose of potassium cyanide, however, proved fatal within two hours. There is, however, the probability of idiosyncrasy to contend with, and poisoning with linseed has been recorded. In one case which I investigated the veterinary surgeon was of opinion that a linseed cake which I found to yield 0·06 per cent. of hydrocyanic acid was the cause of the death of some bullocks, whilst another veterinary surgeon attributed the death of some calves to soaked linseed cake meal which had been given to them, and which I found to yield 0·028 per cent. of hydrocyanic acid.

INSECTICIDES AND FUNGICIDES.—Every year the use of insecticides and fungicides for the control of pests increases, the washing and spraying programme of the fruit and hop farmer, in particular, having been greatly extended. The importance of the amount of the active principle in the preparations used was recognised several years ago, and shortly before 1920 led to a definite demand for legislation. The Chamber of Horticulture and some manufacturers concerned approached the Minister of Agriculture, with the result that a Bill was drafted to ensure that some of the important fungicides and insecticides should be sold only with a guarantee of composition. For certain reasons connected with economy the Bill was never introduced into Parliament. The absence of legislation has led to preparations of varying strength being placed upon the market, and the farmer has, therefore, to take such steps as he may deem desirable to protect himself and to obtain information about the strength of the spray materials which he purchases. Some years ago the Ministry of Agriculture issued a circular setting out the conditions with which some insecticides should comply, and advised purchasers to stipulate that the materials to be purchased must comply with the published conditions. During 1931 a further meeting was held at the Ministry, and the British Insecticide Manufacturers then indicated their willingness to introduce, as a voluntary system, a scheme which would ensure minimum percentages of certain active ingredients in many products. In connection therewith the Ministry undertook to outline a scheme for the testing of proprietary insecticides. At the close of 1931, questions of finance prevented the development of the arrangements. Recently negotiations have been resumed, and it is possible that in the near future standard specifications will be issued.

The numerous materials used for sprays include lime-sulphur solution, lead arsenate paste, nicotine, tar distillate, petroleum, copper sulphate, lime, derris powder, quassia, soft soap, gelatin, etc.

Lime-sulphur solution is generally sold on the understanding, and often with the warranty, that it shall have a specific gravity of 1·3 at 15° C., and that it shall be free from suspended matter. Lime-sulphur, liver-of-sulphur and ammonium polysulphide are usually assumed to depend on polysulphides for their value, and not infrequently the polysulphide sulphur-content of a wash is specified. Invariably the polysulphide sulphur figure specified refers to the percentage of sulphur by weight of liquid, but occasionally a figure is given without stating whether it is W/V or W/W. It is obvious that in a liquid with a high specific gravity, importance attaches to the method of expressing the result. Lime-sulphur probably cannot be marketed with a higher polysulphide sulphur than 21 per cent. W/W. From time to time supplies are sampled which are very weak, but the products of the best manufacturers are consistently good. Methods of analysis of lime-sulphur are given in the Methods of Analysis A.O.A.C., and a very useful direct process for the determination of polysulphide sulphur will be found in the *Journal of Agricultural Science*, 1925, **15**, 96 (ANALYST, 1925, **50**, 148).

Lead arsenate is usually sold in the form of a paste, and these pastes are of varying, though defined, strengths. A minimum standard of not less than 14 per cent. of total arsenic (as As_2O_5) has been suggested. The maximum amounts of water, water-soluble arsenic and of all other impurities have also been suggested. Arsenate of lead is usually known as a stomach poison, that is to say, it kills when it is eaten with foliage, etc., and it is, therefore, essential that arsenate of lead shall exist in a paste in a very fine condition so that it covers as large a superficial area of the foliage sprayed as possible. A rough method to judge the fineness of the arsenate is to make an aqueous suspension and to note the rate of settlement. A guarantee given by one firm states that 97 per cent. will pass the 300-mesh sieve.

Very considerable quantities of nicotine are purchased, particularly by fruit and hop farmers, for spraying purposes, and it is used especially from the middle of May until the end of June. It is very desirable that nicotine supplies should be examined from time to time to note their purity, a common guarantee in England being 96 or 98 per cent. of pure nicotine. Many dry sprays contain nicotine as the active principle, and nicotine in these sprays varies from about

2 to 4 per cent., the absorbents usually being calcium carbonate, calcium oxide or china clay. For certain uses it is very necessary that these dry sprays should be as free from arsenic as possible, and manufacturers have taken great precautions, so that frequently the arsenic content of a dry spray does not amount to more than 1/100 grain per pound.

I do not intend to comment on the many other substances used in the composition of sprays further than to note that the chemist should give some attention to the soft soap so often used as a "spreader." Soda may partly replace potash in a soft soap, with the result that less soap and more water is present, or the fatty acids may be largely replaced by resin acids. The latter acids are objectionable owing to the nature of the curd formed with hard water. Free alkali may cause damage to foliage.

EXAMINATION OF HOPS.—Hops are an important crop in Kent, the cultivated acreage in 1933 being 9366, whilst all the other English counties only had a total of 7529 acres. Last year's crop was estimated to yield 127,000 cwts. of hops, with a probable value of about one and a half million pounds. Hops are usually submitted to the laboratory for determinations of total arsenic, copper and preservative value. Excessive arsenic in hops is invariably due to the presence of coal-ash, the hops having been dried in oasts with open fires. So long as coal (anthracite) almost free from arsenic is used, there is no danger of hops becoming contaminated, but often coals contain appreciable amounts of arsenic, even though they have been obtained from pits which normally yield good coal. A good coal will contain not more than 1/100 grain of arsenic per pound, and when the amount exceeds about 1/50, danger may be apprehended. However, the passage of coal-ash to the drying hops is connected with the draught in the oast. Many oasts are now provided with apparatus which effects drying without the products of combustion reaching the hops. Mineral oil burned in suitable burners is also under experiment as a source of heat for hop-drying. The preservative value of hops is calculated from the determination of soft resins, and a recent process for the determination of these will be found in the *Journal of the Institute of Brewing*, July, 1932, p. 351. Hops in the past have been sold almost entirely on their appearance, but each year we find an increase in the number of buyers who demand a statement about the preservative value of the hops offered. Some copper occurs normally in hops, but the amount may be largely increased if spraying with copper salts takes place after the cones are well formed. Unfortunately, the hop plant may be attacked by a mildew, particularly in wet seasons, which renders spraying essential; but if copper is not used too late in the season, the quantity of copper in the dried hop is certainly of no consequence.

Time prevents me from outlining other investigations undertaken from time to time on behalf of the farmer, but probably I have covered my subject sufficiently to show the value of the agricultural chemist to the farming community.

In conclusion, I feel I may express the thanks of the Society to the Honorary Secretary, Dr. Roche Lynch, to the Honorary Treasurer, Mr. Hughes, and to the Secretary, Dr. Mitchell, for the manner in which the work of the Society has been carried out. I certainly owe a debt of gratitude to all the officers for the help so freely given me on every occasion. The consistent consideration extended to me at all times by Members of the Council and the support afforded to me by Members of the Society I have greatly appreciated, and these have largely contributed to the very happy memories that rest with me of the past two years.

Joint Meeting of the Society with the Food Group of the Society of Chemical Industry

(*Held on February* 7, 1934)

THE following papers were read:

THE ANALYSIS OF FRUIT AND FRUIT PRODUCTS

BY E. B. HUGHES, M.Sc., F.I.C., AND A. E. MAUNSELL, B.Sc.

Fruit, in common with all biological materials, is not a standard product, and therefore anyone concerned with the control of fruit or fruit products from the analytical standpoint must depend for the interpretation of his results on certain standard figures.

When such figures are applied to commercial uses, for example, to judge the quality of fruit puree, either sulphited or not, or of canned fruit, it is obvious that the effect of various factors on the figures must be taken into account. We, ourselves, are but rarely called upon to apply our figures to the examination of jams and such products of unknown origin or composition, but usually apply them to control purchases of fruit and manufacturing processes.

We suggest, however, that the figures, which we have determined over a period of some years, and some of which have already been reported, may be of use to those who require to refer to average figures. It is, perhaps, of importance to state that in most cases we have definite knowledge of the origin of the fruit with which we are dealing, for yearly we send chemists to those areas where fruit is being picked and packed for our own use, to ensure that it is not wet or watery fruit, that its condition is satisfactory, and, if necessary, to make sure that the correct variety is supplied. Samples of the fruit, as collected and despatched, are sent to the laboratory for analysis for record purposes, and also for the checking of deliveries. It is particularly necessary to have such analytical data if the fruit is not to be used at once, but is to be preserved with sulphur dioxide in casks, with or without previous cooking, since to such fruit some water must be added, not only as sulphur dioxide solution, but also because some addition is considered necessary for most fruits to ensure adequate contact of preservative. Another source of water is the washing of fruit before packing, *e.g.* strawberries. Furthermore, analytical data are necessary in the control of the use of the fruit as, for example, in the manufacture of jam, where we control the uniformity of the product by boiling to a specified content of total solids of specified ratio of fruit and sugar. This necessitates the adjustment of the amount of fruit used according to its fruit-content, as determined by analysis, which is particularly necessary when sulphited fruit or canned fruit, such as apricot halves, is used. These requirements indicate that one determination that must be made is the amount of total solids. In addition, knowledge of the amount of sugar is necessary, not only for the obvious reason that it may be an added ingredient, but also because the amount of the natural sugar of the fruits varies (particularly with dry or wet seasons); the amount of sugar in the fruit also may serve as a guide in judging whether or not it had been packed in fresh condition as, if fermentation had taken place to any extent before preserving (in sulphur dioxide or by boiling or processing) this would be indicated by the deficiency in sugar.

The figure which we find to bear the most reliable relationship to the amount of fruit is the difference between total solids and total sugar, *i.e.* the non-sugar solids of the fruit or fruit product; it has also the advantage of not requiring a special determination. In fact, we have found this figure so useful that it may be taken that we do not determine total solids and sugar so much for their direct information as to give us this non-sugar solids result.

Another figure which is so used is, as is well known, the amount of insoluble solids—for which a considerable number of results has been published by Macara (ANALYST, 1931, **56**, 39). We, however, do not make this determination regularly, but such results as we have obtained accord well with Macara's figures. Table I gives the minima, which can be used in determining the amount of fruit in jam, etc.

TABLE I

MINIMUM INSOLUBLE SOLIDS

	A*	B*
Gooseberries	1·66 (7)	1·70 (86)
Strawberries	1·48 (13)	1·30 (47)
Raspberries	4·23 (13)	4·40 (54)
Redcurrants	3·99 (5)	4·05 (9)
Blackcurrants	4·78 (5)	4·70 (20)
Cherries ..	1·29 (6)	0·95 (12)
Plums ..	1·00 (14)	0·75 (14)
Greengages	1·07 (8)	0·95 (5)
Blackberries	6·30 (9)	6·60 (11)
Apricots ..	1·17 (10)	

* Our results, generally fewer, are in column A. * B—Results obtained by Macara (ANALYST, 1931, **56**, 39). Number of samples given in brackets.

The amount of insoluble solids is necessarily much smaller than the non-sugar solids of which it forms part, and it is also more likely to be unevenly distributed in the portioning into jars of a product such as jam. Figures for soluble non-sugar solids would probably be of considerable value to analysts, but we have not sufficient data for statistical selection of such figures.

The methods used for the results given in this paper are described in Appendix A. The only comment here necessary is that, for fruit alone, the method of drying employed gives all the sugar in the total solids in the form of invert sugar, and that, for sweetened fruit products, the method is so modified that the sugars in the total solids remain in the same form as in the sample.

TABLE II

ANALYSES OF SAMPLES OF FRESH FRUITS

Fruit.		Total solids. Per Cent.	Total sugar (as invert sugar) Per Cent.	Non-sugar solids Per Cent.	In-soluble solids Per Cent.	Acidity number (ml. of N/10 per 100 grms.)	Crude calcium pectate Per Cent.	Refractometer reading of juice (sugar scale) Per Cent.
Gooseberries	Max.	14·0	7·7	9·0	2·8	415	1·2	10·1
	Min.	7·9 (51)	2·0 (51)	4·4 (51)	1·7 (7)	176 (36)	0·3 (9)	5·2 (9)
	Av.	11·2	4·4	6·8	2·3	235	0·8	7·0
Strawberries	Max.	13·2	8·2	7·4	2·4	200	0·7	10·2
	Min.	8·2 (145)	3·4 (145)	2·9 (145)	1·5 (13)	90 (125)	0·2 (16)	6·1 (74)
	Av.	10·2	5·4	4·8	1·9	145	0·5	6·6
Raspberries	Max.	21·3	8·7	17·7	6·2	390	0·9	12·3
	Min.	11·0 (107)	3·2 (107)	7·4 (107)	4·2 (13)	106 (90)	0·6 (13)	5·3 (57)
	Av.	14·4	4·8	9·7	5·4	203	0·7	7·9
Redcurrants	Max.	20·7	7·9	17·2	7·8	495	1·5	
	Min.	12·7 (26)	2·2 (26)	7·4 (26)	4·0 (5)	275 (13)	0·9 (5)	
	Av.	16·0	5·0	10·9	5·5	375	1·1	
Blackcurrants	Max.	24·4	10·2	17·7	6·3	622	1·8	14·5
	Min.	13·7 (37)	1·6 (37)	10·8 (37)	4·8 (5)	121 (23)	1·4 (5)	8·0 (5)
	Av.	19·0	5·0	14·1	5·7	449	1·6	11·0
Cherries (Stone-free)	Max.	24·7	15·3	9·8	3·1	145	0·5	18·3
	Min.	10·9 (41)	6·4 (41)	3·3 (41)	1·3 (7)	96 (27)	0·2 (5)	10·0 (10)
	Av.	16·3	10·2	6·1	1·9	107	0·3	13·9
Plums (Various) (Stone-free)	Max.	21·9	13·3	11·7	2·0	386	1·5	22·4
	Min.	8·1 (91)	2·3 (91)	3·4 (91)	1·0 (14)	25 (70)	0·7 (13)	10·0 (36)
	Av.	14·0	7·8	6·2	1·4	215	1·2	14·1
Greengages (Stone-free)	Max.	21·5	13·9	11·8	2·0	435	1·4	19·7
	Min.	11·0 (49)	4·1 (49)	5·1 (49)	1·4 (9)	88 (39)	1·0 (7)	10·2 (14)
	Av.	15·6	7·9	7·8	1·5	189	1·2	16·2
Blackberries	Max.	21·2	10·4	16·0	10·5	206	1·2	11·4
	Min.	14·1 (29)	1·7 (29)	8·4 (29)	6·3 (9)	90 (18)	0·6 (9)	6·5 (12)
	Av.	16·8	4·0	12·8	8·4	135	0·8	8·5
Apricots (Stone-free)	Max.	18·4	11·8	10·4	2·5	349	1·3	18·5
	Min.	8·6 (55)	3·0 (55)	4·1 (55)	1·2 (10)	123 (43)	0·7 (11)	8·0 (24)
	Av.	12·4	5·6	6·8	1·7	235	1·0	12·9
Loganberries	Max.	23·3	7·3	22·2	7·3	420	0·7	
	Min.	13·2 (19)	1·1 (19)	7·3 (19)	7·1 (2)	151 (10)	0·6 (2)	
	Av.	16·6	4·5	12·1		315		
Apples (Whole)	Max.	19·5	13·5	9·8	3·4	410	1·6	17·0
	Min.	10·3 (147)	3·2 (147)	1·1 (147)	1·4 (12)	25 (115)	0·5 (16)	9·8 (39)
	Av.	15·1	10·3	4·9	2·2	162	0·8	13·4
Apples (Edible Portion)	Max.	19·0	14·2	6·9	2·3	450	1·0	17·3
	Min.	11·5 (80)	6·2 (80)	1·4 (80)	1·5 (5)	20 (75)	0·4 (9)	9·8 (38)
	Av.	15·2	10·8	4·4	2·0	93	0·6	13·5
Pears (Whole)	Max.	21·9	12·6	9·9		47		18·6
	Min.	14·6 (22)	7·3 (22)	5·6 (22)		10 (23)		12·0 (18)
	Av.	17·9	10·3	7·6		23		16·0
Pears (Edible Portion)	Max.	20·2	12·8	9·7	1·8	42	0·7	19·2
	Min.	13·5 (23)	7·8 (23)	5·2 (23)	1·7 (3)	13 (25)	0·3 (3)	12·0 (18)
	Av.	17·1	10·5	6·6	1·8	26	0·6	13·2

Number of samples in brackets.

The results which are now given are of the same type as those published by Macara, and are further evidence that such values for fruit show some measure of constancy.

Of these results, the values for pectin and for acidity are of only minor importance in estimating fruit-content. It is known that the natural pectin-content and gel strength of some fruits, notably raspberry (Rendle, ANALYST, **1933**, **58**, 69) and strawberry—particularly in sulphited fruit—suffer very considerable depreciation on keeping the fruit, though this change does not occur appreciably if the fruit is first cooked. Moreover, both pectin and acid may be present as added material.

The only results really of direct use in estimating the amount of a fruit present in a sample are the non-sugar solids and the insoluble solids. It would appear at first sight that the insoluble solids figure is the more satisfactory (or rather less varying), but the following Table (III) gives an idea, as an indication of worth, of the relation of the average figure to the minimum. We have no statistical evidence of the spread of values for insoluble solids, so that this ratio of average to minimum is taken as a rough indication of the degree of variation.

TABLE III

Fruit.	A* Non-sugar solids Average/Minimum	B* Insoluble solids (Macara) Average/Minimum
Gooseberries	$\frac{6·8}{4·4} = 1·5$ (51)	$\frac{2·61}{1·7} = 1·5$ (86)
Strawberries	$\frac{4·8}{2·9} = 1·7$ (145)	$\frac{2·14}{1·3} = 1·6$ (47)
Raspberries	$\frac{9·7}{7·4} = 1·3$ (107)	$\frac{6·17}{4·4} = 1·4$ (54)
Redcurrants	$\frac{10·9}{7·4} = 1·5$ (26)	$\frac{6·02}{4·05} = 1·5$ (9)
Blackcurrants	$\frac{14·1}{10·8} = 1·3$ (37)	$\frac{5·69}{4·7} = 1·2$ (20)
Cherries	$\frac{6·1}{3·3} = 1·8$ (41)	$\frac{1·88}{0·95} = 2·0$ (12)
Plums (Various)	$\frac{6·2}{3·4} = 1·8$ (91)	
(Victoria)		$\frac{1·13}{0·9} = 1·3$ (14)
(Green and Golden)		$\frac{1·03}{0·85} = 1·2$ (5)
(Red)		$\frac{1·22}{0·75} = 1·6$ (15)
Greengages	$\frac{7·8}{5·1} = 1·5$ (49)	$\frac{1·16}{0·95} = 1·2$ (5)
Blackberries	$\frac{12·8}{8·4} = 1·5$ (29)	$\frac{9·64}{6·6} = 1·5$ (11)
Apricots	$\frac{6·8}{4·1} = 1·7$ (55)	
Loganberries	$\frac{12·1}{7·3} = 1·7$ (19)	
Apples (Edible portion)	$\frac{4·4}{1·4} = 3·1$ (80)	

Numbers of samples in brackets. A*—Our results. B*—Macara's figures (ANALYST, 1931, **56**, 39).

The results given in Table III show that the content of non-sugar solids of fruit is of the same order as that of the insoluble solids with regard to the variation in the amount of fruit to be inferred therefrom.

The statistical examination of the figures for non-sugar solids, where we have a sufficient number of results, has been made in our laboratory by Miss B. G. E. Hooke, M.A., and her summarised report is given in Appendix B. Briefly, the examination shows that the distributions for gooseberries and eating-apples (whole) were of symmetrical character, and those for apricots, raspberries and strawberries showed some asymmetry, but gave modal values below the mean values; accordingly, for all these fruits, the distribution of most samples should lie within the limits of mean value ± 2 × standard deviation, and only one sample in 44 would be below the low limit, and only one in 44 above the high limit. Similarly, a value of mean ± 1¼ × standard deviation would give limits of one in ten samples. It is this figure of mean ± 1¼ × standard deviation, the one in ten chance, referred to as probable minimum, which we generally use in calculating fruit-content—chiefly for valuation purposes—but where there is any doubt we use the value for the 43 to 1 chance, which we think sufficiently low, in fact, generously so. The figures for plums and greengages do not come out so well statistically. We think that this is due to bulking varieties of plums and that, for greengages, probably some further separation of varieties is required.

Blackberries require grouping under the headings "wild" and "cultivated." The calculated probable minima for the last-mentioned fruits—plums, greengages and blackberries—are, therefore, apparently somewhat too low.

For currants, the number of analyses is not yet sufficient for satisfactory statistical analysis, but it is reasonably safe to take the probable minima calculated, our evidence having shown that the figure for non-sugar solids of any of the fruits examined has changed but little, as we have been able to add other results from year to year, until the number became really statistically adequate.

TABLE IV

PROBABLE MINIMUM NON-SUGAR SOLIDS

	9 to 1 probability							43 to 1 probability
	1925–7 inc.	1925–8 inc.	1925–9 inc.	1925–30 inc.	1925–31 inc.			
Apples—								
Whole	4·0	3·8	3·8	3·0	3·3	3·5	3·5	2·7
Edible portion					3·2	3·2	3·2	2·5
Apricots	6·5	5·1	5·5	5·0	5·0	5·1	5·2	4·3
Blackcurrants	12·0	12·2	12·4	12·2	12·3	12·3	12·2	11·1
Redcurrants	8·0	7·5	7·9	8·4	8·4	8·4	8·5	7·0
Gooseberries	6·0	6·0	5·7	5·4	5·3	5·4	5·5	4·8
Greengages ..	6·0	5·1	5·3	5·7	5·7	5·9	5·8	4·6
Plums ..	4·0	4·2	4·2	4·2	4·0	4·2	3·9	2·4
Raspberries ..	9·5	8·9	8·7	7·6	7·8	7·7	7·9	6·8
Strawberries	4·5	4·4	4·3	4·0	3·9	3·7	3·9	3·3

Table IV shows the "probable minima" (9 to 1 and 43 to 1) for the samples of various fruits examined in the years 1925 to 1933.

We use these "probable minima" in calculating the amount of fruit in fruit-products, the result being termed maximum fruit-content. Obviously, 100 is the highest figure that can be accorded, unless there is evidence of concentration.

Fruit-composition is influenced by variation in climate and by district. The figures for raspberries in Table V illustrate this.

TABLE V

ANALYSIS OF SAMPLES OF SCOTTISH AND ENGLISH RASPBERRIES (LLOYD-GEORGE VARIETY)

(1930–1932 inclusive)

English					Scottish				
Total solids Per Cent.	Sugars (as invert) Per Cent.	Non-sugar solids Per Cent.	Acidity No. (ml. of $N/10$ per 100 grms.)	Soluble solids (refractometer) Per Cent.	Total solids Per Cent.	Sugars (as invert) Per Cent.	Non-sugar solids Per Cent.	Acidity No. (ml. of $N/10$ per 100 grms.)	Soluble solids (refractometer) Per Cent.
15·4	5·8	9·6	185	10·0	11·0	2·7	8·3	258	8·5
15·5	4·0	11·5	241	10·5	12·0	3·3	8·7	302	8·3
16·8	5·1	11·7	272	10·1	11·8	3·5	8·3	271	7·9
15·6	4·5	11·1	282	9·0	12·5	4·2	8·3	302	8·0
14·9	5·6	9·3	197	12·3	11·4	3·7	7·7	225	6·8
20·5	6·6	13·9	234	10·5	14·2	4·5	9·7	271	8·5
12·5	5·1	7·4	159	8·0	13·5	4·3	9·2	261	8·0
	Av.	10·6				Av.	8·6		
English, 1933					Scottish, 1933				
15·5	6·9	8·6	305	11·0	15·3	4·7	10·6	311	8·7
14·7	3·6	11·1	267	8·0	15·3	6·0	9·3	255	9·4
14·9	5·3	9·6	277	7·5	16·5	6·2	10·3	240	9·9
14·2	5·1	9·0	106	9·0	15·7	5·5	10·2	219	8·4
16·3	6·5	9·8	250	10·1	13·8	4·5	9·3	246	7·7
12·0	3·2	9·8	320	6·9	14·4	5·3	9·0	252	8·3
14·6	5·5	9·1	112	9·2	16·1	6·0	10·1	205	9·1
	Av.	9·6				Av.	9·8		

In the years 1930 to 1932, the samples of Scotch-grown Lloyd-George raspberries had, on the average, lower non-sugar solids than the English fruit, but, in 1933, the results for both were about the same, being between the previous results. In 1931 and 1932, samples of canned raspberry pulp from Tasmania contained appreciably higher fruit solids than English fruit; but, in 1933, the figure fell to the average of English fruit (Table VI). Such variations can be quite important to buyers and users of fruit—both in the value of the fruit and in the standardisation of products.

TABLE VI

AVERAGE NON-SUGAR SOLIDS-CONTENT OF RASPBERRIES

Season	Tasmanian Per Cent.	English Per Cent.
1931	10·3 (10)	9·4 (21)
1932	11·1 (10)	9·9 (20)
1933	9·6 (10)	9·8 (21)

Number of samples in brackets.

The Analysis of Fruit Products.—The methods, which differ in some respects from those employed for fruit alone, are described in Appendix A. The chief differences are in the determination of total solids—it being important to avoid any degree of inversion of the sugar, and, in the determination of sugar, to use methods which are accurate for mixed sucrose and invert sugar.

Canned Fruit (*with or without added sugar*).

Such products are usually simple and contain no other ingredients which might complicate analysis.

The acidity should be in accordance with the fruit-content as calculated from the non-sugar solids. If confirmation of the calculated fruit-content is required, the insoluble solids should be determined, but this is seldom necessary.

TABLE VII

CANNED APRICOTS

	A	B	C
Total solids, per cent.	12·7	8·7	24·0
Total sugars as invert, per cent.	7·4	4·8	—
Invert sugar, per cent. ..	—	—	10·1
Sucrose, per cent.	—	—	10·0
Non-sugar solids, per cent.	5·3	3·9	3·9
Acidity No. (ml. of $N/10$ per 100 grms.)	188	180	181

Interpretation of Results.

Sample A. Maximum fruit-content (9 to 1 probable minimum basis)

$$= \frac{5\cdot3}{5\cdot2} \times 100, \textit{ i.e. } 100 \text{ per cent.}$$

Sample B. Similarly, maximum fruit-content = 75 per cent.

Sample C. Similarly, maximum fruit-content = 75 per cent.

Sample C contains added sugar.

The natural sugar (as invert) for 75 per cent. of fruit would be, taking the average sugar figure of the fruit (5·6 per cent.), 4·2 per cent.

Hence, there is (10·1–4·2) 5·9 per cent. of invert sugar and 10·0 per cent. of sucrose present not due to the fruit, *i.e.* 15·6 per cent. of added sugar as sucrose.

Hence, the sample contains: maximum fruit-content, 75 per cent.; added sugar (as sucrose), 16 per cent. (approx.); added water, 9 per cent.

It is possible that loss of juice from the fruit may occur if, for example, the fruit should have been heated or cooked in water or syrup before filling into containers.

Examples are given in Table VIII.

TABLE VIII

STRAWBERRIES IN SYRUP

	Strawberries	A	B	C	D
Total solids, per cent.	9·3	39·5	22·9	40·1	23·5
Invert sugar, per cent.	5·4	12·5	7·8	12·5	7·8
Sucrose, per cent.	—	24·4	12·5	24·5	12·5
Non-sugar solids, per cent. ..	3·9	2·6	2·6	3·1	3·2
Acidity No. (ml. of $N/10$ per 100 grms.)	118	78	78	78	78
Insoluble solids, per cent.	1·8	1·2	1·2	1·7	1·8

A made from 600 parts by weight of strawberries
300 ,, ,, ,, ,, sugar
B ,, ,, 600 ,, ,, ,, ,, strawberries
300 ,, ,, ,, ,, 50 per cent. sugar syrup
C = A − 300 ,, ,, ,, ,, its syrup
D = B − 300 ,, ,, ,, ,, ,, ,,

Interpretation of:

Sample A. Fruit-content, calculated from insoluble solids

$$= \frac{1{\cdot}2}{1{\cdot}8} \times 100 = 67 \text{ per cent.}$$

Fruit-content, calculated from non-sugar solids

$$= \frac{2{\cdot}6}{3{\cdot}9} \times 100 = 67 \text{ per cent.}$$

Sugar (as invert), natural to the fruit

$$5{\cdot}7 \times 0{\cdot}67 = 3{\cdot}8 \text{ per cent.,}$$

and added sugar (as sucrose) is 32·7 per cent. (33 per cent.).

Sample B. Similarly, fruit-content, calculated from insoluble solids
= 67 per cent.
Fruit-content, calculated from non-sugar solids = 67 per cent.
added sugar = 16·5 per cent.
,, water = 16·5 per cent.

Sample C. Fruit-content, calculated from insoluble solids = 94 per cent.
,, ,, ,, non-sugar solids = 80 per cent.
,, ,, ,, acidity = 66 per cent.

This indicates the presence of not more than 66 per cent. of fruit. Obviously, there has been removal of juice or addition of insoluble solids; the former is the reasonable assumption.

The composition can be calculated as follows:—x = percentage of whole fruit; y = per cent. of insoluble solids, corresponding to juice removed,

$3{\cdot}9x + y = 3{\cdot}1,$
$1{\cdot}8x + y = 1{\cdot}7,$
so that $x = 67$ per cent. of fruit,

$$y = 0{\cdot}5, \text{ corresponding to } \frac{0{\cdot}5}{1{\cdot}8} = 28 \text{ per cent. of fruit.}$$

This is in accordance with the remainder (33 per cent.) being added sugar; the product contains about 67 per cent. of fruit, the insoluble matter of 28 per cent. of fruit and added sugar (about 33 per cent.).

Actually, sample C was obtained from A by draining off 300 parts by weight of syrup from 900 parts of A. A was made from 600 parts of fruit and 300 parts of sugar.

Similarly, sample D is shown to consist of 67 per cent. of fruit and insoluble matter, of 33 per cent. of fruit, and 16·5 per cent. of added sugar. Actually, sample D was obtained from A by draining off 300 parts of syrup (weight) from 900 parts of B.

B was made from 600 parts of fruit and 300 parts of 50 per cent. syrup.

Jam.—For fruits which have no pips, such as "stone" fruits and strawberry, it may be generally sufficient to determine the insoluble solids, though it should be borne in mind that inference of a higher percentage of fruit than required for the grade of the jam should generally result if the fruit-content is calculated from the minimum insoluble solids of the fruit. Should the result even then be somewhat below standard, the possibility must not be overlooked that, in transferring the jam to jars, there may have been unequal distribution of the fruit, resulting in a sample having low insoluble solids. In such a case a full analysis becomes necessary.

For fruits with pips there is always the possibility that some proportion of these have been removed deliberately or skimmed off the jam, thus reducing the insoluble solids. It is also not impossible that pips could be added. Here, again, any doubt necessitates a full analysis; certainly, for adequate criticism of a jam, such full analysis is required, and for this purpose some or all of the following determinations become necessary:

Total solids; sugar (sucrose, dextrose, laevulose, and perhaps glucose syrup; pectin; acidity (titration); p_H; ash; microscopical examination.

The addition of pectin is very common. and allowance, if necessary, must be made for any extra pectin. Acid or acid juice, such as lemon juice, may also be added, and likewise some allowance must be made if the added amount is appreciable. We have made p_H determinations on over 200 samples of various jams which we knew to be free from added acid; in no case have we found a value below 3·1, though we have found instances of commercial jams having p_H values as low as 2·85.

We do not pretend to be in a position to give detailed methods for the estimation of fruit in any or every sample of jam, but the following examples may be of interest and of use.

TABLE IX

	Fresh raspberries	Pectin concentrate	Raspberry jam I made with 40 per cent of these raspberries		Raspberry jam II made with 40 per cent of raspberries + 10 per cent. of pectin concentrate	
	A	B	Analysis	(Composition calculated from A and B)	Analysis	(Composition calculated from A and B)
Total solids, per cent.	11·8	11·5	70·8		70·7	
Sucrose, per cent.	0·0	0·0	28·2		26·3	
Invert sugar, per cent.	3·5	5·8	39·3		40·6	
Non-sugar solids, per cent. ..	8·3	5·7	3·3	3·3	3·8	3·9
Acidity No. (ml. of $N/10$ per 100 grms.)	257	160	103	103	120	119
Insoluble solids, per cent.	5·1	—	2·0	2·0	2·0	2·0
Soluble solids (by refractometer) per cent.	7·9	10·0	70·0		70·1	
Pectin, per cent.	0·7	3·7	0·2	0·3	0·6	0·7

This gives the analyses of two jams and the fruit and pectin used. It will be seen that results accord well.

The composition may be calculated from the "standard" figures as follows (sample II for example).

From insoluble solids, calculated on the basis of the minimum for raspberries:

$$\text{Per cent. of fruit} = \frac{2{\cdot}0}{4{\cdot}4} \times 100 = \text{about 45 per cent.}$$

[From the figure for the average insoluble solids (6·2) only 32 per cent. of fruit would be inferred.]

From Non-sugar Solids.

Non-sugar solids less pectin: $3{\cdot}8 - 0{\cdot}6 = 3{\cdot}2$.

$$\left.\begin{array}{l}\text{Probable minimum}\\ \text{non-sugar solids}\end{array}\right\} - \left\{\begin{array}{l}\text{Average pectin}\\ \text{of raspberries}\end{array}\right\} : 7{\cdot}9 - 0{\cdot}7 = 7{\cdot}2.$$

Hence per cent. of fruit $= \dfrac{3{\cdot}2}{7{\cdot}2} \times 100 = 44$ per cent.

This would indicate added pectin as

$0{\cdot}6 - 0{\cdot}44 \times 0{\cdot}7 = 0{\cdot}29$ per cent. (0·3 per cent.).

The pectin-content of fruits is small, compared with the non-sugar solids, and, consequently, variation in pectin-content is not of great importance in calculations; moreover, pectin, as determined in jam, tends to be rather less than actually originally present in the ingredients used. The other solids of pectin concentrates are usually not present in amounts of importance, considering the quantities used; the accompanying acid may be of importance, but usually the amount so added to the jam will not increase the acidity beyond the ordinary fruit limits; if it does, it must be taken into consideration. An example of this is seen in Table X.

TABLE X

STRAWBERRY JAMS

	A	B
Total solids, per cent.	73·5	73·5
Sucrose, per cent.	26·9	21·9
Invert sugar, per cent.	44·8	49·6
Non-sugar solids, per cent.	1·8	2·0
Acidity No. (ml. of $N/10$ per 100 grms.) ..	63	140
Pectin, per cent.	0·4	0·4
Insoluble solids, per cent.	0·7	0·4
p_H	3·25	2·85

Analyses of 2 samples of strawberry jam.

Sample A.

Fruit-content, calculated from minimum insoluble solids

$$= \frac{0{\cdot}7}{1{\cdot}3} \times 100 = 54 \text{ per cent.}$$

Fruit-content, calculated from average insoluble solids

$$= \frac{0{\cdot}7}{2{\cdot}1} \times 100 = 33 \text{ per cent.}$$

The analysis shows that this sample obviously contains added pectin. The average pectin of strawberries is 0·5 per cent., so that the probable minimum non-sugar solids, less average pectin-content, becomes $3{\cdot}9 - 0{\cdot}5 = 3{\cdot}4$ per cent.

The corresponding figure for the sample is $1{\cdot}8 - 0{\cdot}4 = 1{\cdot}4$ per cent. so that the fruit-content is $\dfrac{1{\cdot}4}{3{\cdot}4} \times 100 = 41$ per cent. This sample would accordingly be passed as in accordance with the Food Manufacturers' Federation standard of 42 per cent. of fruit.

Sample B, which was a commercial product, resembles A in non-sugar solids and in pectin, but differs markedly in insoluble solids, acid number, and p_H.

Calculated from insoluble solids, the fruit-content of the jam is:

$$\text{Taking the minimum: } \frac{0\cdot4}{1\cdot3} \times 100 = 31 \text{ per cent.}$$

$$\text{,, ,, average: } \frac{0\cdot4}{2\cdot1} \times 100 = 19 \text{ per cent.}$$

The acidity is excessive, and, therefore, the non-sugar solids must be corrected similarly, also, allowance must be made for pectin.

The average acidity of strawberries is 145 ml. of $N/10$ acid per 100 grms., equivalent to approximately 1 grm. of citric acid per 100 grms. of fruit.

The average pectin-content of strawberries = 0·5 per cent. Hence: probable minimum non-sugar solids, less average acid, less average pectin, = 3·9—1·0—0·5 = 2·4 per cent., and, for the sample = 2·0—1·0—0·4 = 0·6 per cent. These results indicate $\frac{0\cdot6}{2\cdot4} \times 100$, of fruit, *i.e.* 25 per cent. of fruit.

TABLE XI

THE EFFECT OF REMOVAL OF SOME OF THE PIPS FROM RASPBERRY JAM

	A	B
Total solids, per cent. ..	71·5	71·6
Sucrose, per cent. ..	33·5	33·7
Invert sugar, per cent. ..	35·0	35·3
Non-sugar solids, per cent.	3·0	2·6
Acidity No. (ml. of $N/10$ per 100 grms.)	—	106
Insoluble solids, per cent.	1·7	1·3
Pectin, per cent.	0·3	0·3

These results indicate:

Sample A. Maximum fruit-content (from non-sugar solids, 9 to 1 basis)
= 38 per cent.
,, ,, (from minimum insoluble solids)
= 39 per cent.
Similarly, for *Sample B* : Maximum fruit-content (from N-S.S.) = 33 per cent.
,, ,, (from I.S.) = 30 per cent.

Since, in B, the fruit-content, calculated from *minimum* insoluble solids, is less than that for non-sugar solids, there is indication of loss of insoluble solids.

The F.M.F. standard of 38 per cent. of fruit requires 0·38 × 7·9 = 3·0 per cent. of N-S.S., *i.e.* an increase of 0·4 per cent. over the amount found.

Taking this required increase as insoluble solids, then the amount becomes 1·7 per cent., corresponding to 39 per cent. of fruit.

Both of these samples of jam, A and B, were from the same batch which was prepared so as to contain 38 per cent. of fruit, but, for B, some of the pips had been skimmed from the surface of the hot jam.

It may not be possible to state positively that a single sample of jam is below the declared standard, but examination of a number of samples of that jam, preferably obtained from different shops to give greater chance of their being from different batches of jam, would provide strong evidence for, at least, an intimation to the manufacturer that an explanation is required.

CONCLUSION.—Results have been given of the analysis of a large number of samples of various fruits and, of these results, it is considered that the figures for non-sugar solids are useful in calculating the amount of fruit in such products as canned fruit, jam, etc. For several fruits, sufficient data for non-sugar solids have been obtained to enable statistical examination to be made and probable minima to be calculated. It is suggested that, ordinarily, the probable minima based on: mean — 1½ × standard deviation, representing a 9 to 1 chance that any given sample will not have lower non-sugar solids, should be used to estimate the fruit-content of a sample; where there is doubt, the lower probable minimum: mean — 2 × standard deviation, representing a 43 to 1 chance, might be employed.

This work has been carried out in the laboratories of Messrs. J. Lyons & Co., Ltd., to whom our thanks are due for permission to publish this paper.

METHODS OF ANALYSIS

APPENDIX A

Sampling.—A representative sample of at least 1 lb. is finely minced after fruit stones, stems, etc., have been removed; in the case of the edible portion of apples and pears, the peel and cores are also removed before mincing the sample. The minced sample is finally carefully mixed in a cylinder with a plunger.

Total Solids.—To 1 to 2 grms. of the sample in a nickel dish, hot distilled water is added to distribute the sample evenly over the bottom of the dish. The dish and contents are placed on a water-bath until apparently dry, and finally the remainder of the water is removed by heating in a vacuum-oven at 100° C. for 30 minutes. Experiments have shown that the small quantities of sucrose which may be present in the fruit are inverted during drying. When sucrose is present in appreciable amount, as in jam or canned fruit, the sugars in the dried material are retained in their original form by neutralising (to phenolphthalein) with $N/10$ sodium hydroxide solution before drying. A control determination is made by neutralising citric acid solution of similar acidity with the sodium hydroxide solution and drying in the same way.

Sugar.—Total sugar (as invert sugar) is recorded in the cases of fresh fruit and pulp, since this figure is comparable with the condition of the sugar in the dried solids. Ten grms. of the sample are soaked in hot distilled water for at least 15 minutes, cooled and transferred to a 250-ml. graduated flask. The solution is cleared with 2 to 3 ml. of lead acetate solution (saturated) and 2 to 3 ml. of alumina cream, and made up to the mark and filtered. Any excess of lead is precipitated with solid potassium sulphate and filtered off. Part of the solution is inverted with hydrochloric acid, neutralised, and its copper-reducing power is determined either by the Luff-Schoorl method (*Z. Unters. Lebensm.*, 1929, **57**, 566; *B.C.A.*, 1929, *B.*, 952), or by the Bertrand method. The two methods give identical results.

For jams and fruits to which sugar has been added certain modifications in the method are necessary, as follows:

Ten grms. of the sample are neutralised, and then treated with hot water to dissolve out the sugars, clarified, and made up to 250 ml. Invert sugar is determined, as before, by the Luff-Schoorl sugar method, and laevulose (generally only before inversion) by the Kruisheer iodine laevulose method (*Z. Unters. Lebensm.*, 1929, **58**, 266). The rotatory power of a solution of suitable concentration is compared with that calculated from the determinations made to ascertain whether commercial glucose is present, but this last complication is seldom found.

The correct determination of the actual proportions of sucrose and invert sugar present in the jam, or other sweetened sample, is most important, as otherwise an erroneous result for non-sugar solids will be obtained. The use of the Bertrand sugar method is not advisable, as the presence of sucrose affects the reducing-sugar figure.

Acidity.—Acidity is determined by boiling 10 grms. of the sample with 300 ml. of water for 15 minutes, cooling and titrating to phenolphthalein with N/2 sodium hydroxide solution. These results in our table are expressed as ml. of *N*/10 sodium hydroxide solution per 100 grms. We have found that this method gives results in good agreement with electrometric titration.

Insoluble Solids.—The amount of the insoluble solids is determined by the A.O.A.C. method (*Methods of Analysis*, 2nd Ed., p. 210), except that the final drying is effected in a platinum dish in an oven at 100° C.

Pectin.—The method either of Carré and Haynes (*Biochem. J.*, 1922, **16**, 60) (more generally), and also that of the A.O.A.C. (*Methods of Analysis*, 2nd Ed., p. 212), have been used. Agreement was found to be satisfactory.

p_H Value.—This is determined, where necessary, on a 50 per cent. solution of jam (against *M*/20 potassium acid phthalate solution), with the use of a glass electrode.

Refractometric Reading.—The refractometric reading (on the sugar scale) of the juice, at 20° C., is also recorded (Zeiss refractometer).

APPENDIX B

A variable is said to be distributed normally when it follows a certain mathematical law, that is, the logarithm of the frequency at any distance, x, from the centre of the distribution is less than the logarithm of the frequency at the centre by a quantity proportional to x^2. Such a distribution is symmetrical, with the greatest frequency at the centre, and, although the range is infinite, the frequency falls off rapidly to very small values. The points of inflexion of the curve occur at distances from the centre equal to the standard deviation of the distribution.*

The ratio of the area of the tail of the curve cut off by an ordinate at any point distant x from the centre of the curve, to the total area of the curve, gives the probability that a deviation as great as, or greater than x, is likely to occur. A negative deviation from the mean equal to twice the standard deviation is likely to occur about once in 44 trials, and a negative deviation of 1·25 times the standard deviation will occur about once in 10 trials.

As a test for normality, two quantities $\pm\sqrt{B_1}$ and B_2-3 of Pearson's notation may be calculated. These are both zero for a normal distribution.

From a calculation of these statistical constants for the various distributions of non-sugar solids it was observed that the distribution with eating apples (whole), apricots, and gooseberries approximated most nearly to the symmetrical, while eating apples (edible portion), raspberries, and strawberries and plums, showed some asymmetry with the modal value invariably less than the mean. Except in the case of plums, this asymmetry is not considerable.

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* The S.D. is the square root of the mean square deviation from the mean. Twice the standard error gives the limits of these statistics due to random sampling.

The grouped distributions are shown in Tables, together with their means and standard deviations, the standard errors of these statistics being given also.

The figure obtained by subtracting twice the standard deviation from the mean gives a figure which accords reasonably well with our observations for eating apples (whole), (Table A); eating apples (edible portion), (Table B); apricots (Table C); blackcurrants (Table D); redcurrants (Table E); gooseberries (Table F); loganberries (Table G). The figure for greengages (Table J) is lower than any obtained by analysis; there are 49 observations only, and the distribution is extremely irregular.

Similarly, the figures obtained by this method for pears (whole and edible portion) (Tables L and M) are low. These results are based, respectively, on 21 and 22 observations only.

The distribution for plums (Table N), as mentioned before, shows marked asymmetry, the majority of the observations occurring at the lower end of the distribution, and there being a long tail of high values. An attempt was made, without success, to find a curve which gave a reasonably good fit to this distribution. It may be that there are definite differences in the distribution of certain varieties of greengages and plums, or the irregularities may be partly due to the fact that our selection of fruit for analysis was necessarily arbitrary, and that the distribution cannot be truly said to be random samples.

The figures for cultivated and wild blackberries have been separated (Table O), where the distinction was known. The mean of the former was 11·85, based on 11 analyses, and of the latter, 14·08, based on 10 analyses. Similarly, the mean for red cherries is 5·65 (Table P), as compared with 6·80 and 6·87, respectively, for white and black cherries.

The number of analyses, both of blackberries and cherries, is so few that the calculation of the standard deviation therefrom is of little value.

NON-SUGAR SOLIDS

TABLE A.

Non-sugar solids	EATING APPLES (whole)	COOKING APPLES (whole)
1·005–1·505	1	
1·505–2·005		
2·005–2·505	2	1
2·505–3·005	3	
3·005–3·505	5	2
3·505–4·005	14	1
4·005–4·505	20	3
4·505–5·005	31	1
5·005–5·505	24	2
5·505–6·005	13	1
6·005–6·505	5	3
6·505–7·005	3	4
7·005–7·505	3	2
7·505–8·005		
8·005–8·505	1	
8·505–9·005		1
Total	125	21
Mean	4·78 ± 0·09	5·48
Standard deviation	1·05 ± 0·07	
Mean	1·25SD 3·47	
Mean	2SD 2·68	

TABLE B.

Non-sugar solids		EATING APPLES (edible portion)
2·505–2·755		1
2·755–3·005		1
3·005–3·255		6
3·255–3·505		5
3·505–3·755		9
3·755–4·005		12
4·005–4·255		10
4·255–4·505		7
4·505–4·755		5
4·755–5·005		7
5·005–5·255		2
5·255–5·505		1
5·505–5·755		5
5·755–6·005		1
6·005–6·255		2
6·255–6·505		1
6·505–6·755		
6·755–7·005		1
Total		76
Mean		4·27 ± 0·10
Standard deviation		0·87 ± 0·07
Mean	1·25SD	3·18
Mean	2SD	2·53

TABLE C. APRICOTS

Non-sugar solids	
4·005– 4·505	1
4·505– 5·005	3
5·005– 5·505	4
5·505– 6·005	5
6·005– 6·505	13
6·505– 7·005	8
7·005– 7·505	7
7·505– 8·005	4
8·005– 8·505	4
8·505– 9·005	3
9·005– 9·505	1
9·505–10·005	1
10·005–10·505	1
10·505–11·005	
Total	55

Mean		6·80 ± 0·17
Standard deviation		1·27 ± 0·12
Mean	1·25SD	5·21
Mean	2SD	4·26

TABLE D. BLACKCURRANTS

Non-sugar solids	
10·505–11·005	1
11·005–11·505	
11·505–12·005	2
12·005–12·505	4
12·505–13·005	2
13·005–13·505	1
13·505–14·005	8
14·005–14·505	7
14·505–15·005	3
15·005–15·505	2
15·505–16·005	4
16·005–16·505	1
16·505–17·005	1
17·005–17·505	
17·505–18·005	1
Total	37

Mean		14·07 ± 0·25
Standard deviation		1·50 ± 0·17
Mean	1·25SD	12·19
Mean	2SD	11·07

TABLE E. REDCURRANTS

Non-sugar solids	
7·005– 7·505	1
7·505– 8·005	1
8·005– 8·505	3
8·505– 9·005	
9·005– 9·505	2
9·505–10·005	2
10·005–10·505	2
10·505–11·005	1
11·005–11·505	4
11·505–12·005	2
12·005–12·505	1
12·505–13·005	3
13·005–13·505	2
13·505–14·005	
14·005–14·505	1
14·505–15·005	1
Total	26

Mean		10·94 ± 0·39
Standard deviation		1·98 ± 0·27
Mean	1·25SD	8·46
Mean	2SD	6·98

TABLE F. GOOSEBERRIES

Non-sugar solids	
4·255–4·505	1
4·505–4·755	1
4·755–5·005	
5·005–5·255	2
5·255–5·505	
5·505–5·755	1
5·755–6·005	5
6·005–6·255	8
6·255–6·505	5
6·505–6·755	4
6·755–7·005	2
7·005–7·255	3
7·255–7·505	6
7·505–7·755	1
7·755–8·005	6
8·005–8·255	2
8·255–8·505	1
8·505–8·755	2
8·755–9·005	1
Total	51

Mean		6·80 ± 0·14
Standard deviation		1·02 ± 0·10
Mean	1·25SD	5·52
Mean	2SD	4·76

Table G. Loganberries

Non-sugar solids	
7·005– 7·505	1
7·505– 8·005	1
8·005– 8·505	
8·505– 9·005	1
9·005– 9·505	1
9·505–10·005	
10·005–10·505	1
10·505–11·005	
11·005–11·505	2
11·505–12·005	2
12·005–12·505	2
12·505–13·005	1
13·005–13·505	3
13·505–14·005	
14·005–14·505	2
14·505–15·005	1
Total	18

Mean	11·58 ± 0·50
Standard deviation	2·13 ± 0·35
Mean 1·25SD	8·92
Mean 2SD	7·32

Table H. Raspberries

Non-sugar solids	
6·505– 7·005	1
7·005– 7·505	2
7·505– 8·005	7
8·005– 8·505	14
8·505– 9·005	18
9·005– 9·505	19
9·505–10·005	21
10·005–10·505	8
10·505–11·005	10
11·005–11·505	4
11·505–12·005	7
12·005–12·505	
12·505–13·005	2
13·005–13·505	2
13·505–14·005	4
Total	119

Mean	9·69 ± 0·14
Standard deviation	1·47 ± 0·10
Mean 1·25SD	7·85
Mean 2SD	6·75

Table I. Strawberries

Non-sugar solids	
3·005–3·505	1
3·505–4·005	3
4·005–4·505	16
4·505–5·005	21
5·005–5·505	27
5·505–6·005	40
6·005–6·505	17
6·505–7·005	9
7·005–7·505	9
7·505–8·005	1
8·005–8·505	1
Total	145

Mean	4·83 ± 0·06
Standard deviation	0·76 ± 0·04
Mean 1·25SD	3·88
Mean 2SD	3·31

Table J. Greengages

Non-sugar solids	
5·005– 5·505	2
5·505– 6·005	1
6·005– 6·505	8
6·505– 7·005	4
7·005– 7·505	9
7·505– 8·005	6
8·005– 8·505	2
8·505– 9·005	2
9·005– 9·505	7
9·505–10·005	2
10·005–10·505	3
10·505–11·005	1
11·005–11·505	
11·505–12·005	2
Total	49

Mean	7·75 ± 0·23
Standard deviation	1·59 ± 0·16
Mean 1·25SD	5·76
Mean 2SD	4·57

Table L. Pears (whole)

Non-sugar solids	
5·505– 6·005	2
6·005– 6·505	3
6·505– 7·005	4
7·005– 7·505	1
7·505– 8·005	4
8·005– 8·505	3
8·505– 9·005	2
9·005– 9·505	1
9·505–10·005	1
Total	21

Mean	7·43 ± 0·25
Standard deviation	1·14 ± 0·18
Mean 1·25SD	6·00
Mean 2SD	5·15

Table M. Pears (edible portion)

Non-sugar solids	
5·005–5·255	1
5·255–5·505	2
5·505–5·755	2
5·755–6·005	4
6·005–6·255	1
6·255–6·505	2
6·505–6·755	3
6·755–7·005	1
7·005–7·255	1
7·255–7·505	4
Total	21

Mean	6·35 ± 0·16
Standard deviation	0·72 ± 0·11
Mean 1·25SD	5·45
Mean 2SD	4·91

TABLE N. PLUMS.

Non-sugar solids	
3·005– 3·505	1
3·505– 4·005	3
4·005– 4·505	8
4·505– 5·005	16
5·005– 5·505	14
5·505– 6·005	10
6·005– 6·505	10
6·505– 7·005	5
7·005– 7·505	3
7·505– 8·005	4
8·005– 8·505	5
8·505– 9·005	2
9·005– 9·505	1
9·505–10·005	1
10·005–10·505	5
10·505–11·005	2
11·005–11·505	
11·505–12·005	1
Total	91

Mean	6·23 ± 0·20
Standard deviation	1·90 ± 0·14
Mean 1·25SD	3·85
Mean 2SD	2·43

TABLE O. BLACKBERRIES

Non-sugar solids	Cultured	Wild	?
8·005– 8·505			1
8·505– 9·005			
9·005– 9·505			
9·505–10·005	1		
10·005–10·505	1		
10·505–11·005	1	1	
11·005–11·505	2		1
11·505–12·005	3		2
12·005–12·505	1		1
12·505–13·005			
13·005–13·505		1	
13·505–14·005	1	3	
14·005–14·505		1	1
14·505–15·005		2	1
15·005–15·505			
15·505–16·005	1	1	1
16·005–16·505		1	
Total	11	10	8
Mean	11·85	14·08	12·47

TABLE P. CHERRIES

Non-sugar solids	Red	Black	White
3·005– 3·505	1		
3·505– 4·005	2		
4·005– 4·505	1	1	
4·505– 5·005	5		
5·005– 5·505	1	1	4
5·505– 6·005	3	1	1
6·005– 6·505	2		1
6·505– 7·005	2		1
7·005– 7·505	3	1	2
7·505– 8·005		2	2
8·005– 8·505			
8·505– 9·005			
9·005– 9·505	1		2
9·505–10·005		1	
Total	21	7	13
Mean	5·65	6·87	6·80

THE EXAMINATION OF FRUITS AND JAMS BY LEAD PRECIPITATION*

BY C. L. HINTON, F.I.C.

FOREWORD.—At the time the agreed Jam Standards were introduced, the desirability of extending the methods for determining the fruit-content of jams was discussed by a small committee of the chemists engaged in this industry. Arising out of these discussions, the late L. K. Boseley suggested that the quantity of lead precipitate formed, when a lead acetate solution was added to a solution of a jam, might afford a useful indication of the amount of fruit in the sample, and, as preliminary tests showed that there appeared to be some value in the method, it was decided that the Research Association should investigate it.

This investigation has been carried on during the three past fruit seasons in order to put the process on a satisfactory basis and to obtain suitable data for calculating the percentage of fruit in the jam. It will be seen from what follows that the method will not, by itself, indicate the percentage of fruit in a jam with any more certainty than the other methods already employed; it may be particularly useful in the analysis of jams made from a mixture of fruits, the acids of which differ, *i.e.* one fruit containing citric acid and the other malic. It is also sometimes useful in indicating whether a fruit juice or a commercial pectin has been used in making the jam.

By its use it is possible to place the various fruits in three classes, *i.e.* those containing mainly (i) citric acid, (ii) malic acid, (iii) lactic acid, or an acid having similar lead-precipitating properties.

Mr. C. L. Hinton has been responsible for the carrying out of this investigation, and has drafted the report which follows. The Council of the Association has given permission for the publication of any work of this description which may be of assistance to analysts in maintaining the Jam Standards. T. MACARA

BOSELEY'S METHOD.—The method proposed by Boseley, as mentioned in the foreword, was to dissolve 50 grms. of jam, add 100 ml. of 2 per cent. lead acetate solution, make up to 500 ml., and filter off the lead precipitate together with the insoluble matter of the fruit; 100 ml. of the filtrate were heated to boiling, and the unprecipitated lead was titrated with approximately 1 per cent. ammonium molybdate solution, with tannic acid as an outside indicator. A blank titration was also made on 20 ml. of the lead solution diluted with water. The difference was called the "lead number" of the jam. When the molybdate solution was adjusted in strength to be equivalent, volume for volume, to the 2 per cent. lead solution, the "lead number" represented the number of ml. of 2 per cent. lead acetate solution completely precipitated by 10 grms. of jam.

Essentially this is the procedure still used, though various refinements have been made which will be described later. The "lead number," though empirical, is quite a convenient mode of expressing results, and, as will be seen, is readily linked up with the chemistry of the precipitation.

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* Communicated by the British Association of Research for the Cocoa, Chocolate, Sugar Confectionery, and Jam Trades.

THE NATURE OF THE LEAD PRECIPITATE.—Preliminary experiments on strawberry and raspberry jams of known composition soon showed that the "lead number" was not, as Boseley supposed, a measure of any constituents peculiar to the jam fruits, but was directly related to the amount of acid, both free and in the form of salts, in the jam. In further experiments it was found that malic acid gave no precipitate, whilst citric and tartaric acids gave "lead numbers," on 0·05 grm. of acid, of 6·7 and 6·1, respectively.

A simple calculation shows that, for the complete precipitation of 0·05 grm. of these acids as normal lead salts, 6·8 and 6·3 ml. of 2 per cent. lead acetate solution would be required. Thus, practically within the accuracy of the titration (which is not greater than about 0·1 to 0·2 ml.) these acids seemed to be completely precipitated.

The behaviour of malic acid seemed likely to account for the fact noticed by Boseley, that pomace extracts, etc. (in which most of the acid presumably would be malic) lacked the lead-precipitating constituents of the jam fruits. However, further experiments, described later, showed that the matter was by no means so simple.

IMPROVEMENT OF THE LEAD ACETATE REAGENT.—In experiments in which the acidity of the solution from which the precipitation was made was varied, it was found that in more strongly acid solutions (*e.g.* by adding acetic acid to the jam solution to bring it down to a p_H of 2·5), the end-point of the titration of the excess of lead was upset; but addition of sodium hydroxide to give a p_H of 5·7 caused a slight increase in the "lead number," whilst complete neutralisation of the jam before adding the lead acetate raised the "lead number" about 1 ml. Finally, addition of excess of sodium hydroxide had, as its main result, the precipitation of some, or all, of the excess of lead as hydroxide.

In a series of precipitations of citric acid solution first brought to varying p_H (from 2·5 to 8·0) by addition of sodium hydroxide, it was found that the lead equivalent for 0·08 grm. of citric acid increased gradually over the range mentioned from 11·0 ml. to 12·2 ml., even the lowest figure being rather higher than the theoretical. At the same time the p_H values of the filtrates (tested colorimetrically) were different from those of the original solutions; they were all now compressed into the range 4·4 to 5·6.

In view of this tendency to high results, an attempt was next made to keep down the p_H by means of additions of acetic acid. Mixtures of citric acid and sodium hydroxide (from p_H 2·5 to 8·0, with constant amounts of citric acid) were treated with moderate and relatively large amounts of acetic acid before addition of the lead acetate. The lead equivalents, expressed on 0·1 grm. of citric acid, and also the p_H values, are shown in Table I.

Since the theoretical figure for the lead equivalent of 0·1 grm. citric acid should be 13·55 ml., the results showed that an excess of acetic acid prevented complete precipitation, while a lack of it tended to permit the precipitation of too much lead. In view of these experiments it was decided to adopt a modified reagent prepared by incorporating acetic acid in the lead acetate solution in proportion corresponding with the 2-ml. additions above. Thus the new reagent was composed of:—Lead acetate crystals, 20 grms.; glacial acetic acid, 2·5 grms. per litre.

TABLE I

CONTROL OF LEAD CITRATE PRECIPITATION WITH ACETIC ACID

		2*N* acetic acid added (per 500 ml. of mixture)					
		0 ml.		2 ml.		20 ml.	
Citrate mixture	p_{H} (before addition of acetic acid	p_{H} filtrate	Lead equiv. 2 per cent. lead acetate	p_{H} filtrate	Lead equiv.	p_{H} filtrate	Lead equiv.
I	2·5	4·4	13·8	4·1	13·5	3·6	12·8
II	5·0	5·2	14·3	4·9	13·7	3·9	12·8
III	8·0	5·6	15·2	5·0	13·8	4·0	12·9

DEPENDENCE OF RESULTS ON TOTAL AMOUNT OF PRECIPITABLE ACID.—In tests with the improved reagent it was found that the amount of lead precipitated per unit of acid varied slightly, but definitely, according to the total amount of citric acid present; or, what is almost the same thing, according to the total amount of lead precipitated. Thus, when amounts of citric acid from 0·2 grm. to 0·6 grm. (per 100 ml. of lead solution) were used in the test, the lead equivalents were slightly higher than expected for the smaller amounts of acid, and slightly lower for larger amounts. For the intermediate amounts the precipitation agreed with the theoretical values. Table II gives the actual figures. In preparing the mixtures for precipitation, sodium hydroxide was added to neutralise about one-third of the citric acid, so as to correspond with conditions in fruit extracts.

TABLE II

DEVIATION FROM CORRECT LEAD PRECIPITATION WITH TOTAL AMOUNT PRECIPITATED

Citric acid used (per 100 ml. lead solution) ml.	Calculated titration difference ml.	Titration difference found ml.	Difference ml.
0·20	5·4	5·6	+0·2
0·30	8·1	8·3	+0·2
0·40	10·85	10·9	+0·05
0·50	13·55	13·55	0
0·60	16·25	15·9	−0·35

A few experiments on varying quantities of fruit extracts showed, as was anticipated, that discrepancies were even greater than with citric acid solutions. The results are given in Table III, where the lead equivalents for the varying amounts of fruit extract taken have been calculated in the last column to a common basis of 10 grms., to correspond with the fixed 10 grms. of Boseley's original method.

TABLE III

VARIATION OF LEAD NUMBER OF FRUITS WITH AMOUNT OF FRUIT EXTRACT TAKEN

Fruit	Amt. of 50 per cent. extract represented in titration ml.	Lead titration diff. ml.	Lead number per 10 grms. of fruit ml.
Raspberry	6	7·7	25·7
	8	10·0	25·0
	10	12·0	24·0
	12	14·3	23·8
Gooseberry	4	5·1	25·5
	6	7·3	24·3
	8	9·5	23·8
	10	11·6	23·2
	12	13·7	22·8
Blackcurrant	2	6·7	67·0
	3	9·6	64·0
	4	12·5	62·5
	5	15·1	60·4

In view of these results it seemed necessary to study further the conditions governing the precipitation of the pure fruit acids themselves, both separately and in admixture, and thus establish conditions for correct precipitation when applied to fruit and jam solutions.

CONDITIONS FOR SATISFACTORY PRECIPITATION OF LEAD CITRATE.—It was found more convenient to work with solutions of twice the concentration of those previously used, *i.e.* with 250 ml. instead of 500 ml., and with 50 ml. of filtrate for titration instead of the former 100 ml. In further tests on the precipitation of varying quantities of lead citrate under these conditions, a mono-sodium citrate was used (the total citric-content of which had been determined by titration of free acidity and alkalinity of ash). As before, there was a high result, compared with theory, for the smallest amount of citrate precipitated, and a low result for the largest amount (Table IV). For the intermediate amount, with a lead titration difference of 12 ml., the correct precipitation figure was obtained.

TABLE IV

DEVIATION FROM CORRECT LEAD PRECIPITATION FOR DIFFERENT AMOUNTS OF CITRATE

Monosodium citrate used (per 100 ml. lead solution) grm.	Calculated titration diff. ml.	Titration diff. found ml.	Difference ml.
0·30	8·0	8·2	+0·2
0·45	12·0	12·0	0
0·60	16·0	15·8	−0·2

These figures are similar to those of Table II, except that the deficiency of precipitation at 16 ml. was not so great. This may have been due to the fact that the doubling of the concentration had had some effect.

However, it seemed that correct results were obtainable with citric acid if the total precipitation were such that a lead titration difference of about 12 to 14 ml. was obtained.

BEHAVIOUR OF MALIC ACID IN PRECIPITATION OF MIXTURES.—In preliminary experiments on the precipitation by lead of citric acid, when mixed with malic acid (so as to simulate the conditions in fruit juices), a co-precipitation of part of the malic acid was found, about 40 to 50 per cent. of the theoretical amount of lead being thus precipitated by the malic acid; but the amount was dependent, to an appreciable extent, on the total amount of malic acid present, as well as on the total amount of lead precipitated.

For a more complete investigation, mono-sodium citrate and malic acid of analysed composition were used, and sodium hydroxide was added to the mixtures to keep the p_H in the ordinary range for fruits, *viz.* about 3·5.

In the first series, the citric acid was kept constant, and the amount of malic was varied. In calculating the amount of precipitation due to the malic acid, the effect due to the citric was deducted, with a suitable small allowance for the deviations from correct precipitation already established for that acid. In Table V the effect of the malic acid has been calculated as a percentage of the full amount theoretically precipitable.

TABLE V

PRECIPITATION OF MALIC ACID IN ADMIXTURE WITH CITRIC ACID : CITRIC ACID CONSTANT

Per 100 ml. of lead solution

Amt. of mono-sodium citrate Grm.	Malic acid Grm.	Lead titration diff. ml.	Amt. due to malic acid ml.	Theor. for complete pptn. ml.	Per cent. precipitated
0·35	0·104	10·9	1·5	2·94	51
"	0·208	12·15	2·8	5·89	48
"	0·312	13·35	4·0	8·83	45
"	0·416	14·15	4·8	11·76	41
"	0·520	14·95	5·65	14·72	38

From these results it appeared that the precipitation of the malic acid was relatively less when the total amount of malic (or of malic + citric) was increased; or, looking at it in another way, there was less precipitation of the malic acid as the amount of excess of lead acetate available for its precipitation was reduced.

A second series was tried in which the malic acid was kept constant, but the citrate was varied. Again, in calculating the amount of precipitation due to the malic acid, allowance was made for the slight variation in the citric acid effect (Table VI).

TABLE VI

PRECIPITATION OF MALIC ACID IN ADMIXTURE WITH CITRIC ACID : MALIC ACID CONSTANT

Per 100 ml. of lead solution

Amt. of mono-sodium citrate Grm.	Malic acid Grm.	Lead titration diff. ml.	Amt. due to malic acid ml.	Theor. for complete pptn. ml.	Per cent. precipitated
0·20	0·298	8·85	3·35	8·43	40
0·30	"	11·75	3·75	"	45
0·40	"	14·35	3·75	"	45
0·50	"	16·4	3·2	"	38

Under these conditions the malic acid precipitation again varied, reaching a maximum when the lead titration difference was from 12 to 14 ml., or under about the same conditions (as regards excess of lead) as for the correct precipitation of citric acid.

In a third series the total amount of precipitation was kept approximately constant (by varying the proportions of citrate and malic acid) at about this point of correct citric and maximum malic precipitation (Table VII).

TABLE VII

PRECIPITATION OF MALIC ACID IN ADMIXTURE WITH CITRIC ACID : TOTAL LEAD PRECIPITATION CONSTANT

Per 100 ml. of lead solution					
Amt. of mono-sodium citrate	Malic acid	Lead titration diff.	Amt. due to malic acid	Theor. for complete pptn.	Per cent. precipitated
Grm.	Grm.	ml.	ml.	ml.	
0·40	0·178	13·2	2·55	5·04	51
0·35	0·296	13·2	3·9	8·38	46
0·30	0·415	13·2	5·2	11·75	44
0·25	0·543	13·15	6·5	15·36	42
0·20	0·661	13·0	7·7	18·71	41
0·15	0·780	12·8	8·8	22·08	40

This series showed again the effect of increasing quantities of malic acid, as in Table V, so that this effect is manifested over and above the effect noted from Table VI, since it occurs when all the lead precipitations are at what should be the point of maximum malic acid precipitation.

The practical outcome of these experiments was that, if the quantity of malic and citric acids were kept within suitable limits, the malic acid precipitated could be taken as a fixed percentage. In particular, if the malic acid used in the test (per 100 ml. of lead solution) amounted to at least 0·3 grm., and the citric acid was from about 0·2 grm. to 0·3 grm., about 40 to 45 per cent. of the malic acid was precipitated. A mean figure of 43 per cent. can be taken to cover all such cases correctly, within the limits of experimental error.

Subject to these restrictions, we have a means of determining the proportion of malic acid in a mixture of the two acids (or their salts). For this purpose it is convenient to reckon all the acid as citric acid (this total acid is ascertainable directly from titrations of free acidity and of ash, when salts are present). Then the theoretical amount of 2 per cent. lead acetate solution, equivalent to each 0·1 grm. of acid (as citric), is 13·55 ml. But whilst all the citric acid is precipitated, only 43 per cent. of the malic acid accompanies it.

Thus, if T be the grms. of total acid present in the solution used for the test; D the lead titration difference (*i.e.* on one-fifth of T); and M the grms. of malic acid (reckoned as citric) contained in the T grms. of total acid,

$$D = \frac{13{\cdot}55}{0{\cdot}1}\left[\frac{1}{5}M \times \frac{43}{100} + \frac{1}{5}(T - M)\right]$$

$$= 27{\cdot}1\,[T - 0{\cdot}57\,M],$$

whence $M = 1{\cdot}75\,T - 0{\cdot}065\,D$ .. .. (I).

To take an illustration, suppose the total of the two acids in a solution taken for the test is 0·75 grm., reckoned as citric, and that the lead titration difference is 12·8 ml., then

$$M = 1{\cdot}75 \times 0{\cdot}75 - 0{\cdot}065 \times 12{\cdot}8 = 0{\cdot}48 \text{ grm.}$$

and the citric acid would be $0{\cdot}75 - 0{\cdot}48 = 0{\cdot}27$ grm.

The actual malic acid, as malic, would be $0{\cdot}48 \times \frac{67}{70} = 0{\cdot}46$ grm.

It will be noted that the quantity of each of the acids conforms to the restrictions previously set out. It may sometimes happen that this is not so. In that case, in order to obtain a more accurate result, the determination should be repeated, with suitable additions of either citric or malic acid, as the case may require, and, if necessary, also an accompanying alteration in the amount of the mixture taken for the test.

The titration difference may fall outside the range of 12 to 14 ml. required for correct precipitation of the citric acid. In that case a small correction, based on the data of Tables II and IV, may be applied before calculating the proportions of malic and citric acids. These corrections are given in Table VIII.

TABLE VIII

CORRECTIONS TO BE APPLIED TO LEAD TITRATION DIFFERENCES

Lead titration diff. ml.	Correction ml.
8·5— 9	−0·2
9·1—11	−0·1
11·1—14	0
14·1—15	+0·1
15·1—16	+0·2

Titration values outside the range shown here are less reliable, and, when obtained, a fresh determination on an altered quantity of original solution should be made.

BEHAVIOUR OF PECTIN IN THE LEAD PRECIPITATION.—Before applying the method elaborated for pure acids to fruit extracts it was thought desirable to examine the behaviour of pectin when precipitated by lead.

A solution of orange pectin, containing 0·82 per cent. of pectin as calcium pectate, was used. The free and combined acidity of the pectin, expressed on the calcium pectate basis, was equivalent to 13·6 per cent. as citric acid. Thus, for theoretical precipitation of the pectin as the lead salt, 100 ml. of pectin solution would require 13·55 × 0·136 × 0·82 ml. = 15·1 ml. of 2 per cent. lead solution.

In a first experiment, in which 100 ml. of the pectin solution were treated alone by the usual procedure, the titration difference was 2·9 ml. This was, as usual, on one-fifth of the total volume, so that the theoretical lead equivalent should have been $\frac{15{\cdot}1}{5} = 3{\cdot}02$ ml. Within ordinary limits, therefore, the precipitation result was in agreement with the theoretical value.

In a subsequent experiment, 125 ml. of pectin solution were mixed with a known amount of citric acid solution (partly neutralised with sodium hydroxide to correspond with conditions in a fruit juice). The titration difference was 12·8 ml., whilst a control test of the citric acid solution, without the pectin, gave 10·6 ml., or a difference of 2·2 ml., due to the pectin. The theoretical lead equivalent should have been $15{\cdot}1 \times \frac{1{\cdot}25}{5} = 3{\cdot}8$ ml., so that, in presence of citric acid, the precipitation of lead by the pectin was reduced considerably.

The amounts of pectin used above were four or five times as large as would be present in the test as carried out on an ordinary fruit or jam, but, in order to prevent any possible interference, and also to improve the filtration, which tended to be sluggish in the presence of the pectin, a preliminary treatment with acetone was introduced into the procedure to remove the pectin. A fruit or jam extract was made up to double its volume with acetone, being meanwhile swirled round to avoid entangling too much air, and then filtered, with precautions against evaporation. A suitable amount of this pectin-free filtrate was taken for the test, and, after removal of the acetone by evaporation, the solution was cooled, and the lead test proceeded with as usual. The free and combined acidity of the fruit were also determined on the pectin-free filtrate, so that all results should be on the same basis.

EFFECT OF PHOSPHATES ON LEAD NUMBER.—In view of the effect of the possible (though doubtful) presence of small amounts of phosphates in fruit extracts or jams, known amounts of a solution of acid potassium phosphate (KH_2PO_4) were added to citric acid solutions, and the mixtures were treated by the usual lead process. In Table IX the quantities taken, and lead titration differences found, are shown; and the effect due to the phosphate, obtained by deducting that of the citric acid, is compared with the theoretical amount required for the complete precipitation of triplumbic phosphate [$Pb_3(PO_4)_2$].

TABLE IX

PRECIPITATION OF LEAD BY PHOSPHATE IN ADMIXTURE WITH CITRIC ACID

Citric acid taken Grm.	KH_2PO_4 taken Grm.	Lead titration diff. ml.	Amt. due to phosphate ml.	Theoretical for phosphate ml.
0·10	0·30	15·9	13·3	12·54
0·20	0·20	13·7	8·3	8·36
0·30	0·10	12·2	4·1	4·18

The precipitation was close to the theoretical value. It should be noted that any phosphate present in a fruit extract would behave, in the determination of free and combined fruit acids, as though it were the salt of a dibasic acid, *e.g.* $KH(HPO_4)$, whereas the lead salt precipitated is the tribasic salt. Thus, any part of the apparent "total fruit acid" which may be present as phosphate would appear to precipitate 3/2 times the amount of lead that would be precipitated by its equivalent of citric acid. Thus, whilst 0·1 grm. of citric acid (equivalent weight = 70) has a 2 per cent. lead acetate equivalent of 13·55 ml., 0·1 grm. of phosphoric acid (virtual equivalent in fruit analyses = 49) has a lead equivalent of

$$13{\cdot}55 \times \frac{70}{49} \times \frac{3}{2} = 29{\cdot}0 \text{ ml.}$$

The phosphoric acid in the ash of a large number of samples of fruit has been found to be usually between 0·03 and 0·06 per cent. of the fruit. Since the lead number of the fruit, by Boseley's scheme, is expressed on 10 grms. of sample, that portion of it due to this phosphoric acid would be $29 \times \frac{0{\cdot}003}{0{\cdot}1} = 0{\cdot}9$ to 1·8 ml, if it were present as phosphate in the fruit extract. This, however, is doubtful, at least as regards the whole of it; so that the effect of any phosphate in this way would not be great, and certainly very much less than the natural variations in lead number from one sample of fruit to another.

BEHAVIOUR OF OTHER ACIDS IN THE LEAD PRECIPITATION.—Although the evidence discussed later indicates that citric and malic acids are the principal acids occurring in jam fruits, at least in quantity sufficient to affect significantly the amount of lead precipitate, the effect of a few other acids has been studied.

Tartaric Acid.—This is, of course, a prominent acid in the grape, but does not occur to any extent in most jam fruits. A few experiments with a solution of cream of tartar of known composition showed that this acid was precipitated as neutral lead tartrate when submitted to the standard "lead number" process (see Table X).

TABLE X

LEAD PRECIPITATION OF TARTARIC ACID

Tartaric acid* taken (per 100 ml. of lead solution) Grm.	Calculated titration diff. ml.	Titration diff. found ml.	Diff. ml.
0·298	7·5	7·7	+0·2
0·447	11·3	11·4	+0·1
0·596	15·0	14·7	−0·3

* *i.e.* equivalent to the amount of cream of tartar taken.

The slight differences from the theoretical values are very similar to those of citric acid, so that, in the event of tartaric acid being present, the corrections given for citric acid (Table VIII) would apply. There would be no interference with the calculation of the malic acid present in a mixture of the three acids.

Succinic Acid.—Tests carried out on succinic acid in admixture with varying proportions of mono-sodium citrate showed that there was no more lead precipitated than would be due to the citrate alone.

Thus, any succinic acid present in a mixture of fruit acids would cause the amount of malic acid, as given by the calculation earlier, to be too high. However, no definite evidence has so far been found that succinic acid occurs in any appreciable quantity in jam fruits.

Fumaric Acid.—This acid has been stated to occur as a natural constituent of some fruits.

Experiments on the lines of those already carried out with malic and succinic acids showed that fumaric acid, when citrate was also present, precipitated lead to the extent of about 55 per cent. of the amount required to form the neutral lead salt. Thus, any fumaric acid present would appear as malic acid in the calculation of the latter.

However, attempts to identify fumaric acid in extracts of plums and greengages, in which its presence was at first suspected for other reasons, gave negative results.

Lactic Acid.—This acid is not supposed to occur naturally in fruits, though it may be considered as a natural "food" acid, and is in some countries officially recognised as a permissible substance in food preparations. It is used in the manufacture of some commercial pectin preparations, which, therefore, introduce it into jams containing them.

Experiments on lactic acid alone, and also in admixture with citrate solutions, showed that there was no precipitation of lead whatever by the lactic acid. Thus, any lactic acid present in fruit products would considerably increase the apparent amount of malic acid, as given by the calculation from the lead precipitation. Since the calculation depends on the fact that 57 per cent. of the malic acid is unprecipitated, whereas the whole of the lactic acid remains so, the latter would cause the malic to appear too high by $\frac{100}{57}$ times its equivalent weight as malic acid. In the presence of lactic acid, therefore, the method of calculating malic acid breaks down, unless there is some means of determining the former and allowing for it.

AN EXTENSION OF THE LEAD PRECIPITATION PROCESS: PRECIPITATION FROM 50 PER CENT. ACETONE SOLUTION.—Auerbach and Weber (*Z. anorg. Chem.*, 1925, **147**, 68), in the course of a general study of the solubility of the lead salts of fruit acids, found that the lead salts (of citric, malic, tartaric, and succinic acids) were only very slightly soluble in 50 per cent. alcohol. This seemed to hold out the possibility of more definitely characterising the individual acids and the fruit extracts, etc., in which they were present, and an extension of the lead-precipitation process was accordingly devised.

Acetone seemed to offer advantages over alcohol as a medium for the new form of precipitation, and a few preliminary experiments showed that the lead salts were just as insoluble in a 50 per cent. (by vol.) acetone medium as in the alcohol mixture of Auerbach and Weber. The amount of lead precipitated by citric acid was, however, about 10 per cent. more than the theoretical, whilst malic acid now gave practically the same precipitation as citric acid, also about 10 per cent. more than the theoretical. It is possible that this extra precipitation of lead is connected in some way with a shift of p_H caused by the acetone (as shown when an indicator was added). It was found in the experiments of Table I that when the p_H is not controlled in the aqueous precipitation, excess lead, up to at least 12 per cent., was precipitated.

In the aqueous precipitations it was found that correct precipitation of lead by citric acid was obtained when about 0·5 grm. of citric acid was taken per 100 ml. of 2 per cent. lead acetate (see Tables II and IV). The precipitation in the acetone medium was more arbitrary, and there was no point at which it could be said that "correct" precipitation was obtained. Hence, for the purpose of comparisons and practical work, it was decided to assume that the precipitation given by 0·5 grm. of citric acid (per 100 ml. of lead solution) was a "correct" one for the acetone medium. This was found to average 15·0 ml. of lead-titration difference. On this basis the actual results found for citric acid and a number of mixtures of malic and citric acids, in the acetone medium, are compared in Table XII with the calculated "correct" values. In these tests, as in previous ones, the citric acid was used in the form of mono-sodium citrate, and the malic acid in the partially neutralised condition, to correspond with the conditions in fruit products.

TABLE XII

DEVIATION FROM ASSUMED CORRECT LEAD PRECIPITATION IN 50 PER CENT. ACETONE MEDIUM

Per 100 ml. of lead solution

Mono-sodium citrate Grm.	Malic acid Grm.	Calc. lead titration diff. ml.	Titration diff. found ml.	Difference
0·30	—	8·85	9·15	+0·3
0·45	—	13·26	13·35	+0·1
0·60	—	17·7	17·2	−0·5
0·35	—	10·3	10·7	+0·4
0·35	0·104	13·6	13·65	+0·05
0·35	0·208	16·8	16·5	−0·3
0·20	0·298	15·25	15·05	−0·2
0·30	0·298	18·2	17·4	−0·8
0·40	0·074	14·1	14·2	+0·1
0·35	0·123	14·15	14·3	+0·15
0·30	0·173	14·25	14·3	+0·05
0·25	0·222	14·3	14·3	0
0·20	0·271	14·35	14·4	+0·05
0·15	0·321	14·45	14·45	0

The precipitation due to the malic acid in the mixtures has been assumed to be the same as for the equivalent amount (*i.e.* $\times \frac{70}{67}$) of citric acid.

It can be seen that the lead equivalents of the acids present are subject to the same sort of slight fluctuations as in the aqueous precipitations. The deviations increase rather sharply with titration differences above about 16 ml., probably owing to insufficient excess of lead.

It should be noted that the deviations shown by the solutions containing malic acid were similar to those of citric acid alone. This means that the malic acid is precipitated as completely from the 50 per cent. acetone medium as is citric acid.

In Table XIII the deviations are expressed in the form of corrections which can be applied to the titration differences to bring them all to the same basis of assumed correct precipitation.

Titration differences falling outside the above range are not very reliable; in such cases it would be advisable to repeat the test with a different amount of the solution.

When the titration differences have been corrected in this way, the sum of the citric and malic acids (both expressed as citric) in a mixture of the two can be found by taking a titration difference of 15·0 as representing 0·10 grm. of acid (as citric) precipitated; or, what is the same thing, 0·50 grm. of acid in the full quantity of solution taken for precipitation by the 100 ml. of 2 per cent. lead acetate solution.

TABLE XIII

CORRECTIONS TO BE APPLIED TO LEAD TITRATION DIFFERENCES (PRECIPITATION IN 50 PER CENT. ACETONE)

Lead titration diff. ml.	Correction ml.
9·0—11	—0·3
11·1—13	—0·2
13·1—14	—0·1
14·1—15	—0
15·1—15·7	+0·1
15·8—16·2	+0·2
16·3—16·5	+0·3
16·6—16·8	+0·4
16·9—17·1	+0·5

Thus, suppose 25 ml. of a solution are treated with 100 ml. of 2 per cent. lead acetate, and the mixture is made up to 250 ml. with acetone and filtered; 50 ml. of the filtrate are then titrated and found to give a difference from the blank of 12·5 ml. The correction on this, from Table XIII, brings it to 12·3 ml. Hence, the amount of combined citric and malic acids in the 25 ml. of solution initially taken is $0{\cdot}5 \times \frac{12{\cdot}3}{15{\cdot}0} = 0{\cdot}41$ grm. (expressed as citric acid).

BEHAVIOUR OF OTHER ACIDS IN THE 50 PER CENT. ACETONE MEDIUM.—Tartaric acid, which, it was seen, is precipitated completely, like citric acid, from aqueous solution, is precipitated similarly to citric acid from the 50 per cent. acetone, *i.e.* a slight excess of lead being thrown out (about 15 per cent.). As this acid is not present to any extent in jam products, no significant error arises if the lead equivalent of the citric acid is used to cover both acids. Thus, the acid precipitated in acetone includes tartaric with the citric and malic acids.

Phosphoric acid (used in the form of KH_2PO_4) was found to precipitate from the 50 per cent. acetone medium just the theoretical amount of lead required for the triplumbic phosphate. There was no excess precipitation as with the organic acids. However, it must be remembered that the same consideration holds good as in the aqueous precipitation of phosphate; any of the fruit acidity due to phosphoric acid, as given by titration to the phenolphthalein end-point, has 3/2 times the lead-precipitating power of the organic acids. Consequently, if phosphoric acid is present in a mixture, the total lead precipitation from acetone will be higher than it would be if all the acids were organic.

Fumaric acid (examined in admixture with citrate), precipitated practically the theoretical amount of lead from the acetone medium, but there was a slight solubility effect, as a slight further precipitate came out from the filtrate, on standing overnight. In any case, this acid would be included with sufficient accuracy in the total of the other acids.

Lactic acid, both alone and in admixture with citrate, was found to be unprecipitated from the acetone medium. This was a fact of special importance. It was shown earlier that, when present, this acid, owing to its non-precipitation from aqueous solutions, invalidates the calculation of malic acid. In the acetone medium, however, it was alone among the acids considered here in not being fully precipitated. Hence, we have a ready means of estimating its amount with some exactness, and so allowing for its effect in calculating the malic acid.

If T be the grms. of total acid in the solution used (obtained as before mentioned by titration of the free acidity and of the ash), D′ the lead titration difference for the 50 per cent. acetone medium (*i.e.* on one-fifth of T), and K the grms. of lactic acid (reckoned as citric) in the T grms. of total acid, then we have

$$D' = \frac{15\cdot 0}{0\cdot 1} \times \frac{1}{5}(T - K),$$

since 0·1 grm. of citric acid (or its equivalent in malic, tartaric, etc.) precipitates 15·0 ml. of 2 per cent. lead acetate solution. From this equation,

$$K = T - \frac{D'}{30} \qquad \cdot\cdot \quad \cdot\cdot \quad \cdot\cdot \quad \cdot\cdot \quad \cdot\cdot \qquad \text{(II)}$$

Reverting to the earlier equation (I) for the calculation of the malic acid from the aqueous lead titration difference, the T in that equation must now be replaced by (T–K), since the lactic acid was completely inert in that determination also. So we have $M = 1\cdot 75\,(T - K) - 0\cdot 065\,D$,

or, substituting for K the value given by equation (II) above,

$$\begin{aligned} M &= 1\cdot 75\,(T - T + \frac{D'}{30}) - 0\cdot 065\,D \\ &= 0\cdot 058\,D' - 0\cdot 065\,D \qquad \cdot\cdot \quad \cdot\cdot \quad \cdot\cdot \qquad \text{(III)} \end{aligned}$$

Thus, the malic acid can now be obtained by a simple calculation from the two lead titrations. It may be noted that, for the purpose of determining the malic acid only, it is not necessary to know the total acidity of the solution; this is only required if the lactic acid, or the total acid (citric + tartaric + phosphoric) are required in addition.

It should be pointed out that the preceding calculation includes any phosphoric acid with the citric acid, and assumes that it precipitates lead similarly to the latter. Actually, as was shown earlier, this is not the case. The effect of the assumption is to make the calculated amounts of lactic and malic acids slightly low, whilst the remaining acid (*i.e.* citric + tartaric + phosphoric) is made slightly high. The errors, even supposing that all the phosphorus found in the fruit ash is derived from phosphates, are not very large—not more than 0·02 per cent. (expressed on the fruit) for the malic, and 0·035 per cent. for the (citric + tartaric + phosphoric) acids.

The above method for determining the malic acid breaks down, of course, if there are appreciable amounts of other acids present which are differently precipitated in aqueous and in acetone medium. From other evidence it seems likely that such is not the case with many fruits, including most of the soft jam fruits and apples. With regard to stone fruits there is more doubt. In any case, for the purpose of the analysis of fruit products there seems no objection, in the first instance, to classing empirically as malic acid all the acid material which behaves like it in the lead tests. This device, while ignoring the slight errors that may be caused by traces of phosphoric or other acids, has the advantage, from an analytical standpoint, of separating the acid constituents of the fruits into three groups:

(i) Citric acid, and acids which behave similarly (*e.g.* tartaric acid); (ii) malic acid, and acids which behave similarly (if any); (iii) lactic acid, and acids which behave similarly (if any).

Since it will be shown later that the acids of apples and of the stone fruits consist chiefly of malic acid (or of acids behaving like it), it is clear that a means of discriminating between the different groups of acids affords useful information in the analysis of mixed products.

DETERMINATIONS OF LEAD NUMBER ON FRUIT EXTRACTS.—In the course of the past two or three seasons a considerable number of determinations of lead number has been made on extracts prepared from fresh fruits. At first the aqueous extracts were used for the precipitations without removing the pectin, but it was found later that the results with stone fruit were more reliable if the pectin was removed. Later determinations were, therefore, always carried out on the filtrate from the precipitation of pectin with acetone, the acetone being removed by evaporation prior to the aqueous lead precipitations. It was found that results on this pectin-free filtrate were practically identical with those on the original extract of soft fruits and apples, but were sometimes different (usually higher), and certainly more reproducible, with the stone fruits. Later, when the lead precipitation from 50 per cent. acetone was worked out, the procedure was arranged so as to take advantage of the preliminary precipitation of the pectin with the acetone, as will appear in the description of the full method of working eventually adopted.

A further modification introduced when the acetone lead precipitation came into use was a fivefold increase in strength of the lead acetate solution (including the contained acetic acid); in place of the former 100 ml., only 20 ml. of the stronger solution were, of course, used. This permitted of the use in the test of sufficiently large amounts of the rather weakly acid extracts obtained from some samples.

Also, for stone fruits and apples, the practice was adopted in the aqueous precipitations of adding a suitable amount of citric acid (in the form of monosodium citrate solution or of the free acid) in order to ensure the proper co-precipitation of the malic acid (see BEHAVIOUR OF MALIC ACID, p. 251). A still later improvement was the addition to some extracts, where the natural malic acid was believed to be deficient (as in strawberries, raspberries, etc.), of small amounts of malic acid, also for the purpose of securing the right degree of co-precipitation. Appropriate allowance was made for these additions of citric or malic acid in calculating the lead numbers of the fruits.

In Table XIV is given a summary of the results of determinations of the aqueous lead number on most of the ordinary jam fruits. For stone fruits and apples only the later results, obtained on pectin-free extracts, and with additions of citrate as above mentioned, are included. The extracts of the fruits were prepared by boiling the samples with an equal weight of water for an hour, cooling, replacing the water lost by evaporation, and filtering. In calculating results back to the original fruit, correction has been made for the amount of insoluble matter, and also for the fact that the extracts were made up by weight, whilst the amounts used for analysis were pipetted. The lead numbers are expressed according to Boseley's original scheme, *i.e.* the number of ml. of 2 per cent. lead acetate solution precipitated by 10 grms. of the sample.

In addition to the lead numbers, the table shows the average total acid-content of each kind of fruit (from the free acidity and ash titrations). Finally, the value obtained by dividing the lead number of each sample by its total acidity is shown. This is really the lead equivalent (2 per cent. lead acetate solution) of each 0·1 grm. of acid (as citric acid). It is also numerically equal to the "lead number per 1 per cent. of acid" in the sample. If all the acid were citric acid, this figure would be 13·55. The deviation from this is a measure of the proportion of non-precipitated or partly-precipitated acids (probably chiefly malic acid) present.

The figures for "highest" (and "lowest") values of lead numbers and of lead number per 0·1 grm. of acid do not necessarily belong to the same sample.

TABLE XIV

LEAD NUMBERS OF JAM FRUITS (AQUEOUS PRECIPITATION)

Fruit	No. of samples		Lead number ml.	Total acidity, as citric acid Per Cent.	Lead number per 0·1 grm. acid ml.
Gooseberries ..	17	Highest	29·9	—	11·7
		Lowest	17·3	—	9·5
		Average	25·5	2·44	10·4
Strawberries ..	15	Highest	22·7	—	13·3
		Lowest	9·8	—	10·5
		Average	16·3	1·31	12·4
Raspberries ..	11	Highest	34·2	—	14·3
		Lowest	19·0	—	12·1
		Average	26·8	2·02	13·3
Redcurrants ..	7	Highest	43·1	—	14·3
		Lowest	34·8	—	12·0
		Average	37·6	2·81	13·4
Blackcurrants ..	10	Highest	64·8	—	14·4
		Lowest	39·5	—	12·2
		Average	52·7	3·92	13·5
Apples	4	Highest	10·9	—	7·4
		Lowest	6·9	—	6·3
		Average	9·4	1·33	7·1
Plums	5	Highest	18·0	—	7·6
		Lowest	6·9	—	2·5
		Average	10·2	2·14	4·8
Greengages ..	2	1.	12·0	—	5·9
		2.	8·1	—	5·5
		Average	10·1	1·77	5·7
Damsons ..	4	Highest	19·4	—	7·0
		Lowest	9·4	—	3·0
		Average	13·0	2·77	4·7
Blackberries ..	12	Highest	22·5	—	10·2
		Lowest	7·2	—	8·1
		Average	13·9	1·51	9·2
Apricots ..	2	1.	20·8	—	11·0
		2.	14·7	—	9·6
		Average	17·8	1·72	10·3

From these results it appears that the acid of raspberries, redcurrants and blackcurrants is almost entirely citric acid (or belongs to that type). Strawberries contain a slight proportion of other acid, gooseberries, blackberries, and apricots rather more, whilst apples and the stone fruits probably contain very little citric acid.

In a few analyses of raspberries and currants the value for the lead number is even slightly higher than should be obtained if all the acid precipitated its full equivalent of lead. Part of this excess may be due to difficulty in determining the end-point of the titration, which is sometimes found in the more strongly coloured fruits; but part may be also due to traces of phosphates, which, it will be remembered, precipitate lead more strongly than their titratable acidity warrants.

The results of lead-number determinations in the 50 per cent. acetone medium are summarised in Table XV. The data are fewer, as this method was only brought into use during the 1932 season. This accounts for the slightly different average figures for acidity compared with those of the preceding Table.

TABLE XV

LEAD NUMBERS OF JAM FRUITS (50 PER CENT. ACETONE PRECIPITATION)

Fruit	No. of samples		Lead number ml.	Total acidity, as citric acid Per Cent.	Lead number per 0·1 grm. acid ml.
Gooseberries ..	2	1.	40·9	—	15·4
		2.	39·8	—	15·4
		Average	40·4	2·62	15·4
Strawberries ..	3	Highest	27·0	—	15·6
		Lowest	15·8	—	15·3
		Average	21·4	1·39	15·4
Raspberries ..	3	Highest	37·4	—	15·6
		Lowest	35·0	—	15·0
		Average	36·6	2·38	15·4
Redcurrants ..	2	1.	51·8	—	17·1
		2.	50·7	—	16·7
		Average	51·3	3·04	16·9
Blackcurrants ..	2	1.	78·2	—	17·3
		2.	74·1	—	16·3
		Average	76·2	4·53	16·8
Apples	4	Highest	22·2	—	15·1
		Lowest	16·5	—	14·9
		Average	19·9	1·33	15·0
Plums	3	Highest	34·4	—	14·6
		Lowest	19·0	—	12·3
		Average	26·1	1·88	13·9
Greengages ..	3	Highest	28·6	—	13·0
		Lowest	15·0	—	10·3
		Average	20·3	1·68	12·1
Damsons ..	2	1.	43·3	—	15·6
		2.	34·9	—	14·6
		Average	39·1	2·59	15·1
Blackberries ..	2	1.	34·4	—	15·6
		2.	22·2	—	15·2
		Average	28·3	1·84	15·4
Apricots ..	2	1.	25·9	—	15·3
		2.	23·5	—	13·6
		Average	24·7	1·72	14·4

In most of the fruits it is evident that the lead number in the acetone medium was very close to that corresponding to complete precipitation of the acids. That is to say, the acids fall into the citric or malic acid groups. Most of the results were a little higher, in fact, as can be seen by comparing the "lead number per

0·1 grm. of acid" with the theoretical figure of 15·0. With currants the precipitation was appreciably higher than this; so far a satisfactory explanation has not been found, but it is possible that phosphates partly account for the excess.

The most interesting results were from plums and greengages. The few samples of these examined all gave incomplete precipitations, showing the presence of some acid not belonging to either the malic or citric acid groups. The behaviour of this acid in the lead tests, according to the scheme elaborated in an earlier section, was similar to that of lactic acid. Whether it is lactic acid or not is a matter as yet undecided. Unfortunately, its amount is apparently very variable, so that it does not offer very much prospect of assistance in discovering the fruit-content of products containing these fruits.

DISTRIBUTION OF THE ACID GROUPS IN FRUITS.—If the equations (II) and (III) given earlier are applied to the two sets of lead numbers obtained from the fruits, approximate figures for the amount of each of the three acid types are obtained. This has been done for all those samples for which determinations of both lead numbers were available, and the apparent amounts of the malic acid and lactic acid types, expressed as percentages of the total organic acid, are shown in Table XVI. Many of the percentages so found, especially of "lactic acid," are slightly negative. This may possibly arise from the presence of traces of phosphate,

TABLE XVI

APPARENT PROPORTIONS OF ACIDS OF DIFFERENT TYPES IN FRUIT SAMPLES

Fruit	Total acid Per Cent.	Per cent. of total acid	
		Malic acid group	Lactic acid group
Gooseberry	2·65	41	− 3
	2·58	35	− 3
Strawberry	1·76	15	− 2
	1·39	8	− 3
	1·01	14	− 4
Raspberry	2·39	− 5	− 4
	2·48	− 2	0
	2·27	12	− 3
Redcurrant	2·97	16	−14
Blackcurrant ..	4·54	5	− 9
	4·51	14	−15
Apple	1·47	78	0
	1·42	81	0
	1·31	77	0
	1·10	92	0
Plum..	1·75	93	5
	1·55	70	18
	2·35	70	3
Greengage	2·20	80	13
	1·38	70	17
Damson	2·78	90	− 4
	2·39	97	2
Blackberry	2·21	67	− 4
	1·46	47	− 1
Apricot	1·54	53	− 2
	1·90	15	9

which would affect the calculation of both the malic and lactic acid types in a negative direction (see p. 259). Larger negative results are shown by currants, which, it was seen, had a tendency to give lead numbers above the theoretical in the aqueous precipitation, and quite notably above it in the acetone precipitation.

Apple and the stone fruits appear as predominantly "malic acid" fruits, whilst gooseberries, blackberries and, perhaps, apricots, appear to have a more even distribution of the acids in the citric and malic groups.

Some of these findings, so far as relative proportions of citric and malic acids are concerned, are similar to the results of Nelson (ANALYST, 1924, **49**, 592; 1925, **50**, 191, 295), who made a direct determination of the acids by an ester distillation method. He found in strawberries 10 per cent., raspberries 3 per cent., blackberries 17 per cent., and apricots 70 per cent. of the total acid to be malic acid. Franzen and Helwert (*Z. physiol. Chem.*, see *Canning Age*, 1925, June, p. 562) reported the acids of apples to be chiefly malic, with some citric; whilst currants contained chiefly citric, with some malic acid. This, again, is confirmed by the present results.

THE LEAD NUMBER OF JAMS.—We return, finally, to the motive behind Boseley's original idea of the lead-precipitation process, namely, the desire for a means of arriving at the approximate fruit-content of jams.

It has been shown that the lead number is due certainly (within experimental limits of accuracy) to the acid constituents of the fruits; further, that the acid constituents themselves can, by means of the lead precipitation, be separated into groups, and that the fruits fall broadly into classes containing a preponderance of citric or malic acid. Thus, it should be possible, within certain rough limits, to discover whether the acid constituents of a jam are normal to the class of fruit used, provided that any foreign fruit or fruit juice added belongs to a different class. In particular, the addition of apple pulp or juice, or pomace extract, to strawberry, raspberry, etc., jam, should make itself evident by disturbing the normal citric acid preponderance of these fruits. On the other hand, such additions to stone fruit jams would not appreciably alter the proportions of the acid groups (unless use can ultimately be made of the "lactic acid" group).

For the present the discussion will be confined to the former case. For this purpose it is not necessary to calculate from the lead number the actual quantities of citric and malic acids present. The lead numbers themselves can be used and compared with established data for the several kinds of fruits concerned, with due allowance for the natural variations. It should here be pointed out, what is evident from Tables XIV and XV, that it is not the lead number itself that is specially characteristic of a particular fruit. Thus, a lead number of 6·5 found for a jam might be given by 40 per cent. of strawberries alone, or by 25 per cent. of strawberries and 26 per cent. of apple pulp, or by 60 per cent. of apple alone. The characteristic property which makes it possible to gain some idea of the proportions of the constituents in such mixtures is the lead number *relative to the acid content*, or, according to the empirical method adopted above for expressing this property, the "lead number per 0·1 grm. of acid." (It should be remembered that *total* acid is always meant here, as obtained from the free acidity and ash titrations.) Hence, from a consideration of the average values for this figure for the fruits concerned, their respective proportions in an unknown mixture, or rather, the proportions of their acids, can be approximately determined.

The matter may be made clearer by an example. Suppose the "lead number" of a strawberry and apple jam to be 6·4, and the percentage of total acid in the jam was found to be 0·61, then the acid in the 10 grms. of jam equivalent to the 6·4 ml. of 2 per cent. lead acetate solution is 0·061 grm., and the "lead number per 0·1 grm. of acid" is $\frac{6{\cdot}4}{0{\cdot}61} = 10{\cdot}5$. Now the averages for strawberries and apples are, respectively, 12·4 and 7·1 (Table XIV). Hence the proportion of the acids due to strawberries is $\frac{(10{\cdot}5 - 7{\cdot}1)}{(12{\cdot}4 - 7{\cdot}1)}$ 100 per cent. of the total, = 64 per cent. Thus, the percentage of acid in the jam due to strawberries is $0{\cdot}61 \times \frac{64}{100} =$ 0·39 per cent.; and that due to apples will, therefore, be 0·61 − 0·39 = 0·22 per cent. Taking the average total acid contents of strawberries and apples as 1·31 per cent. and 1·33 per cent., respectively (Table XIV), the amounts of the two fruits in the jam are:

$$\text{Strawberry: } \frac{0{\cdot}39}{1{\cdot}31} \times 100 = 30 \text{ per cent.}$$

$$\text{Apple} = \frac{0{\cdot}22}{1{\cdot}33} \times 100 = 17 \quad ,,$$

The same method can be applied to other mixtures, provided the characteristic figures for the fruits concerned, "lead number per 0·1 grm. of acid," are sufficiently far apart. Thus, the method breaks down for such mixtures as raspberry and redcurrant, plum and apple, etc., and is of doubtful value for blackberry and apple, or strawberry and gooseberry (see Table XIV).

The calculation can be expressed in the form of a simple formula.

Let F_1 and F_2 be the respective percentages of two fruits in a mixed product,

L_1 and L_2 the average values of the "lead number per 0·1 grm. acid" (Table XIV),

A_1 and A_2 the average values for total acid in the two fruits (Table XIV),

l the actual "lead number per 0·1 grm. of acid" found in the sample,

and a the actual per cent. of total acidity found,

$$\text{Then } F_1 = \frac{100a(l - L_2)}{A_1(L_1 - L_2)} \quad \cdots \quad \text{(IV)}$$

$$\text{and } F_2 = \frac{100a(L_1 - l)}{A_2(L_1 - L_2)} \quad \cdots \quad \text{(V)}$$

Jams containing Pomace Extracts or Pectins.—Most jams now on the market contain added pectin, which is used either in the form of a direct extract from pomace, or a specially-prepared proprietary "fruit pectin" (usually prepared from apple residues), or as a dry powdered pectin prepared from citrus fruits or apple residues. The latter preparations, which are more or less pure pectin, should introduce no lead-precipitating acids but themselves into the jam; and, as they can be removed along with the natural fruit pectins by a preliminary precipitation with acetone, they should cause no complications.

The case is different with pomace extracts, etc. These, when they are aqueous extracts, may be considered as apple extracts deprived of a portion of their natural acids. The remaining acids, however, will still have the same lead-precipitating properties as the acids of the whole fruit (apart from the pectinous constituents, which can be removed before the lead test is made). Thus, the formulae of the preceding section can still be applied, though the apparent percentage of apple juice indicated will be low because of the removal of part of its acid. There will be no interference with the calculation of the amount of the main fruit constituent (F_1).

Some commercial pectins, however, appear to have been prepared by an extraction of pomace with lactic acid. Two of the most popular "fruit pectins" on the market in this country, for instance, on examination by the lead process, both in the aqueous and the 50 per cent. acetone medium, showed a large proportion of lactic acid (or an acid of closely similar type) among their acid constituents. Table XVII shows the essential parts of the analysis of these products, and the proportions of citric, malic, and lactic acid groups calculated from the lead numbers by the formulae already given.

TABLE XVII

COMPOSITION OF ACID CONSTITUENTS OF COMMERCIAL PECTINS AS CALCULATED FROM THE LEAD NUMBERS

		Lead number (per 10 grms. of sample)		Acids (expressed as citric)		
Sample	Total acid (as citric) Per Cent.	Aqueous medium	50 per cent. acetone medium	"citric" acid Per Cent.	"malic" acid Per Cent.	"lactic" acid Per Cent.
A.	2·04	3·0	6·9	0·05	0·41	1·58
B.	1·09	3·7	8·7	0·05	0·53	0·51

Thus, in one case about half, and in the other case three-quarters of the acid was lactic acid, the remainder being, presumably, the natural acids of the apple still remaining in the pomace or apple residues used.

Clearly the calculation of the fruit-content from the aqueous lead number by formula (IV) would be erroneous in jams containing such pectin preparations. The effect of the lactic acid would be to depress the "lead number per 0·1 grm. of acid," making the proportion of apple acids appear too high. The solution of the difficulty is afforded by the second, or "acetone" lead number. This gives a value for the total acids excluding the lactic acid, so that a corrected value can be obtained for the "lead number per 0·1 grm. of acid," which refers only to the malic and citric types of acid. Formula IV can then be applied to these corrected values for a and l.

This calculation is of use only for those fruits which themselves show no appreciable amount of the lactic type of acid, *viz.* the soft fruits and damsons (see Table XVI). But, as plums and greengages have an aqueous lead number so similar to that of apples as to preclude its use in calculating fruit-content in their case, the restriction is not a material one.

It is desirable to point out here, in connection with the calculation of fruit-content in mixtures containing commercial pectins, that experience in the analysis of a large number of jam samples of various origin has shown the figure of 7·1 for the "lead number per 0·1 grm. of acid" of apples (Table XIV) to be rather high for general application. This was the average from four samples only. A figure giving results more in accordance with other analytical indications is 6·5. This, too, is about the figure given by the commercial pectins of Table XVII, when due allowance is made for the extraneous lactic acid.

Hence, for the fruit-content of jams with added "pectin" (from apples), formula IV may be simplified to:

$$F_1 = \frac{100a(l - 6{\cdot}5)}{A_1(L_1 - 6{\cdot}5)} \qquad \ldots \quad \ldots \quad \ldots \quad \text{(VI)}$$

The a and l of this formula should be suitably corrected for any lactic acid shown to be present by the "acetone" lead number. Values of A_1 and L_1 appropriate to the various fruits may be obtained from Table XIV.

DETAILS OF ANALYTICAL PROCEDURE.—The details of the procedure adopted for the various determinations involved in applying the lead-precipitation method to the analysis of jams are as follows:

Preparation of Extract.—Weigh 250 grms. of the sample into a beaker, and add 250 ml. of water. Mix well to break up the jam, then heat to boiling with continual stirring, and boil gently for an hour, with occasional stirring, keeping the beaker covered, and maintaining the volume by adding water, if necessary. Cool, transfer to a 500-ml. measuring flask, make up to volume, shake well, and filter through a coarse filter.

Preparation of Pectin-free Filtrate.—Transfer 250 ml. of the aqueous extract to a 500-ml. flask, and add acetone (while swirling round without entangling too much air) to the mark. Mix well, and filter through a large dry filter, with precautions to avoid loss by evaporation.

Titration of Free Acid.—Pipette 40 ml. of the pectin-free filtrate into a large beaker, add about 500 ml. of boiled and cooled distilled water, and titrate with $N/10$ sodium hydroxide solution, using phenolphthalein as indicator. Carry out a blank titration of 500 ml. of the water similarly, and deduct this from the jam titration. The difference, multiplied by 0·07, gives the percentage of free acid (expressed as hydrated citric acid) in the jam.

Ash of Jam.—Evaporate 50 or 100 ml. of the pectin-free filtrate to dryness in a platinum dish on a water-bath, char over an Argand burner (protecting the contents of the dish from the gas fumes), and ash at a dull red heat, preferably in an electric muffle. Cool and (if required) weigh.

Titration of Combined Fruit Acid.—Dissolve the ash in a measured 15 ml. of $N/10$ hydrochloric acid, filter into a 175-ml. conical flask, and wash through thoroughly. Boil for a few minutes. Cool, add a drop of methyl orange solution, titrate to yellow with *N*/10 sodium hydroxide solution, and then to the neutral tint with *N*/10 hydrochloric acid. Calculate the amount of acid consumed by the ash to the number of ml. of *N*/10 acid per 100 grms. of jam; this is the "methyl orange alkalinity" of the ash. (Pfyl, *Z. Nahr. Genussm.*, 1922, **43**, 313.)

Next acidify the titrated solution with about 2 ml. of *N*/10 hydrochloric acid, and evaporate to about 15 ml. (It is sometimes advisable to boil on a sand-bath, on account of bumping.) Cool, and neutralise carefully to methyl orange with *N*/10 sodium hydroxide solution. Add a few drops of phenolphthalein solution and 10 ml. of a strong neutral calcium chloride solution. Boil again for a few minutes, and titrate to the phenolphthalein end-point with *N*/10 sodium hydroxide solution. Calculate the number of ml. of *N*/10 sodium hydroxide solution per 100 grms. of jam, and multiply by 3/2. This gives the phosphoric acid in the ash as its equivalent of *N*/10 sodium hydroxide solution. Then find the "total alkalinity" of the ash, equivalent to all the alkali and alkaline earth metals present, by adding to the "methyl orange alkalinity" one-third of the phosphoric acid equivalent. Finally, multiply this total alkalinity by 0·007 to obtain its value as percentage of combined fruit acid as citric acid.

Total Fruit Acid.—The total fruit acid (including any phosphates present in the extract) is the sum of the free acid and combined acid found as above, and is expressed as the percentage of total citric acid (hydrated).

Aqueous Lead Number.—Take an amount of pectin-free filtrate (to the nearest 5 or 10 ml.) containing approximate amounts of total fruit acids according to the following scheme:

	Grm.
(i) Gooseberry, apricot, or blackberry jams	0·50
(ii) Strawberry, raspberry, redcurrant, or blackcurrant jams ..	0·35
(iii) Apple, cherry, plum, greengage, or damson jams	0·65

Remove the acetone by distillation, transfer the residue to a 250-ml. measuring flask, and cool. Then add, in the case of groups (i) and (ii), 3·0 ml. of 10 per cent. malic acid solution, or, in the case of group (iii), 3·0 ml. of 5 per cent. citric acid solution (pipetted accurately). (The strength of the acid used should be correct to within 1 per cent. of the total.) Dilute to about 200 ml. Ensure that the temperature of the solution is at about 16° to 20° C., then add from a pipette, while rotating the flask, 20 ml. of lead acetate solution (containing 100 grms. of normal lead acetate pure crystals, and 12·5 grms. of glacial acetic acid, per litre), and make up to volume with water. Shake well, and filter without delaying more than a few minutes. Titrate 50 ml. of the filtrate (diluted with 50 ml. of water) at or near the boiling-point, with ammonium molybdate solution (9·3 grms. per litre), using a 0·5 per cent. solution of tannic acid as an outside indicator (by spotting on a tile). The first appearance of a distinct yellow colour in the test drop (or a definite increase in a slight existing yellowish colour) marks the end-point.

For a blank titration, dilute 20 ml. of the lead acetate solution to 250 ml., and titrate 50 ml. of this + 50 ml. of water in the same way. Correct the difference between the two titrations for any lack of correct strength in the lead or molybdate solutions. If the difference so corrected is not in the range 11–14 ml.. make a further correction according to Table VIII. (Should the difference lie outside the range there allowed for, repeat the determination on a larger or smaller quantity, as the case may require, of pectin-free filtrate.)

From the corrected titration difference deduct 3·6 ml. (when malic acid was initially added) or 4·1 ml. (when citric was added). Calculate the remainder back to the number of ml. of 2 per cent. lead acetate solution, which would be completely precipitated by 10 grms. of the original sample (or 40 ml. of the pectin-free filtrate). This is the "lead number" (aqueous) of the jam, according to Boseley's original definition; that is, if the amount of pectin-free filtrate taken for the test be P ml., and the corrected titration difference D, then

$$\text{Lead number (aqueous) } L = \frac{200D}{P}$$

The "lead number per 0·1 grm. of acid" is then found by simply dividing L by the percentage of total fruit acid (a) in the sample

$$l = \frac{L}{a} \qquad \ldots \quad \ldots \quad \ldots \quad \text{(VII)}$$

Acetone (50 *Per Cent.*) *Lead Number.*—Take an amount of pectin-free filtrate (to the nearest 5 or 10 ml.) containing approximate amounts of total fruit acid as follows:

		Grm.
(i)	Gooseberry, strawberry, raspberry, redcurrant, blackcurrant, apricot, or blackberry jams	0·50
(ii)	Apple, cherry, plum, greengage, or damson jams	0·40

(If more than 200 ml. would be required, the amount must be restricted to this figure.)

Place the required amount in a 250-ml. measuring flask, and in the case of jams of group (ii) add 3·0 ml. of 5 per cent. citric acid solution (measured accurately). (Should it have been necessary to limit the amount of pectin-free filtrate taken to 200 ml., the deficiency of fruit acid may be made up by a suitable addition of 5 per cent. citric acid solution, its effect being allowed for later.)

Add acetone, while rotating the flask, to make up the total amount of acetone present to 125 ml. Then add from a 20 ml. of 10 per cent. lead acetate solution (as in the aqueous test), and make up to volume with water. Mix, and filter, taking precautions to avoid loss by evaporation. Titrate 50 ml. of the filtrate, diluted with 50 ml. of water, as in the aqueous test.

Correct the difference between the titration and the blank (that obtained earlier will suffice) for any factors of the lead or molybdate solutions. If the difference so corrected is not approximately 14–15 ml., make a further correction according to Table XIII.

From the corrected titration difference deduct 1·5 ml. for each 1 ml. of added 5 per cent. citric acid solution, if any.

Calculate the remainder, as before, back to the number of ml. of 2 per cent. lead acetate solution completely precipitated by 10 grms. of the sample. This is the "lead number" (acetone) L′ of the jam. The lead number per 0·1 grm. of acid is then obtained as before,

$$l' = \frac{L'}{a} \quad \ldots \quad \ldots \quad \ldots \text{(VIII)}$$

Interpretation of Results.—If l' is appreciably less than 15, and plums or greengages are not present, lactic acid from a commercial pectin is probably present, and its amount can be approximately found by a formula adapted from the equation (II) given earlier:

$$k = a - \frac{L'}{15} \quad \ldots \quad \ldots \quad \ldots \text{(IX)}$$

where k is the percentage of lactic acid in the sample. A corrected value for l (see VII) is then obtained by deducting the lactic from the total acid:

$$l\,(\text{corrected}) = \frac{L}{a - k} \quad \ldots \quad \ldots \quad \ldots \text{(X)}$$

The value for l, corrected or not as required, and the total acidity a, with any lactic acid deducted, are then used in formula VI to find the fruit-content of the sample.

For mixed jams coming within the scope of the method, formulae IV and V may be used, though it should be noted that if pomace extract or liquid pectin is present, it will be included with the fruit of lower lead number.

DISCUSSION

The PRESIDENT remarked that all would agree with him that they had had very interesting papers read to them, and that the methods described were extremely ingenious, and the results of unquestionable utility. They had now agreed standards for the fruit-content of jam, and also the National Mark Standards were in existence, and it was, therefore, very essential that any proposed methods of analysis by means of which the true fruit-content of jam could be determined should be closely studied. He himself had had practically no experience of the examination of fresh fruits, and this must be the case with many other analysts, and, therefore, the results which Mr. Hughes and Miss Maunsell had given would be of great value. He admired the ingenuity those authors had displayed in the method of calculation. They had concluded their paper by observing that it was really necessary to examine a number of jams before coming to any definite conclusion. The Public Analyst usually had to draw his results from one sample, and this was perhaps unfortunate. He was particularly pleased to hear Mr. Hinton's paper because, as Mr. Hinton had mentioned, Boseley had experimented with a lead process, and almost on the last occasion on which he was present at a meeting of the Society he had referred to his process which he enthusiastically believed would enable the fruit-content of jam to be accurately determined.

Mr. T. RENDLE congratulated the Society on having such an excellent evening, and the authors on papers containing such useful information. All who handled fruit and fruit products had felt the lack of satisfactory methods of analysis, and every fresh figure was a considerable help. He would like to know whether the figures for apricots referred to the fresh, dried or canned fruit. He believed that Macara's published figures for insoluble solids showed very considerable differences for different varieties of the same fruit, and for the same variety grown in different districts. Mr. Hughes and Miss Maunsell had put forward figures for one variety only of raspberries—"Lloyd George." He felt that it would add to the value of the paper if further information on other varieties could be given, and if the maximum and minimum figures, as well as the average, were included. He would also like to know whether there was less variation between the maximum and minimum values for non-sugar solids than with the figures for insoluble solids on the same samples.

With regard to Mr. Hinton's paper, it was customary in the manufacture of pectin from pomace to adjust the final acidity by the addition of citric or tartaric acid. Would the use in a jam of pectin containing these acids influence the lead number?

Mr. G. N. GRINLING referred to a pamphlet issued by the Research in Canning Section of the University of Bristol, whereby the ingredients of canned fruit were calculated.

Mr. J. R. NICHOLLS queried how accurate the figure for non-sugar solids was likely to be. Presumably, when one got differing total solids and sugars, all the errors would be thrown on the non-sugar solids.

Mr. YOUNG asked what was the possibility of the action of sulphites on the lead number.

Mr. WILSON (from California) said what a great pleasure it had been to him to be present at that meeting. He had done some work on these lines himself, and certainly, in California, they found that many factors, such as degree of ripeness, variety and district, affected these natural products. It was always a pleasure to him to attend such a meeting, and he extended a hearty welcome to any member who could attend one of their meetings in America.

Dr. L. H. LAMPITT said that when a mass of figures, such as those they had had that evening, was shown upon the screen it was practically impossible, at the time, seriously to consider them and put forward any useful criticism. He did not know whether Mr. Hinton had considered the large number of other acids which occurred in small quantities and how far they were likely to affect his results of mixed acids when found in jams. Knowing how interested Mr. Boseley had been, Dr. Lampitt thought that it would be a very good thing if chemists in the fruit trade could try this method on a large number of samples. It was only by gradual accumulation of a large number of figures that they were likely to get satisfactory information of a biological nature. He would like to thank Mr. Hinton for putting forward another possible tool which might prove of great use.

Mr. T. MACARA congratulated Mr. Hughes and his colleague on the very ingenious way in which they had worked out the value of the non-sugar solids in fruits and applied the results to the analysis of jams. He had given figures in his own paper on the "Composition of Fruits" (ANALYST, 1931, **56**, 39), from which the non-sugars could be calculated, and although these figures were not obtained by the same methods, they could be used in the way indicated by Mr. Hughes and Miss Maunsell. It was a pity that the Society had not found it possible to publish all the tables of analyses of fruits which he had submitted, as the results for individual fruits were frequently helpful in dealing with difficult cases. He hoped that the new results would prove helpful to others. He was pleased to hear the authors stress the necessity for the examination of more than one sample before coming to a decision. This was necessary to meet cases of bad distribution of the fibre and seeds in filling the jam into jars. There were also occasions when a manufacturer was obliged to skim off seeds or pips when these floated too freely to the surface of the jam. There were, of course, other cases where pips might be deliberately added, and it was then necessary to consider other constituents of the fruit, *e.g.* the acid. In this connection he referred to the case of a sample of gooseberry and raspberry jam submitted to him for analysis. This contained sufficient pips to represent 100 per cent. of raspberries, but he had reported it as containing only 10 per cent. At first the manufacturer professed indignation at this result, but afterwards admitted that he had purposely "faked" the jam to see whether it could be detected. He stated that he had added 12 per cent. of raspberries. The result reported was arrived at after a consideration of the figures for constituents other than that for insoluble matter, particularly the acid figure, in conjunction with a microscopical examination. It must be recognised, however, that it was possible to make a report of this sort for commercial purposes, when a Public Analyst might naturally hesitate to do so. He was not quite sure that the authors fully realised the Analyst's position in this respect.

Mr. Hinton's paper described another very useful method. Like all other methods proposed, it could not, by itself, give the true fruit-content of a jam. It was, however, another tool which did help, especially with jams made from a mixture of fruits containing different acids.

Mr. A. L. BACHARACH said that he would like to add his tribute to the ingenuity of the calculations. During the last few years he had become increasingly impressed by the practical value of statistical methods. Mr. Hughes and Miss Maunsell that evening had done one extremely useful thing (among others) by showing that, in fact, these methods could be employed to give certain figures and results that were perfectly intelligible, and gave one the only really sound basis for the control of many manufacturing processes.

Miss MAUNSELL, replying to Mr. Rendle, said that the apricots referred to in the tables were fresh fruit, except in Table VII, where canned apricots provided the data for an example of calculation. For all fruits, the analyses of many varieties were included, and the non-sugar solids figures for each kind of fruit fell into the statistical distribution calculated. The fruit was obtained from England, Scotland, Holland, Germany, Belgium, France, Italy, and (in the case of apricots) Spain. South African apricots also contained non-sugar solids in agreement with the figure for English and Spanish fruit. The same applied to South African and American apples and pears. With regard to the question about varieties of raspberries, and whether they varied according to district, "Lloyd George" raspberries had been selected to illustrate the difference between those grown in England and those grown in Scotland. Different varieties of this fruit did not vary very much; one obtained, possibly, high results for one season, but all the varieties would give high results for that district. All varieties of raspberries fell within the limits given, and so varieties could not be differentiated by chemical analysis. The pamphlet mentioned by Mr. Grinling was of interest, but the results were based on physical data; it might be helpful to use both sets of figures.

As to limits of accuracy: in Table IX the calculated composition of the jam was given, as well as the actual analysis, and it would be seen there that the greatest difference in non-sugar solids was 0·1 per cent., *viz.* non-sugar solids, 3·9 per cent. calculated and 3·8 per cent by analysis.

Mr. HINTON, replying, said that the citric or tartaric acid used in extracting pectin had no appreciable disturbing effect. He did not think that, bearing in mind the small amounts used, the amounts of acid would fall outside the range of natural variations in the fruits. Mr. Young mentioned the possibility of disturbance by sulphites. Sulphite was quite easily dealt with by boiling the sulphur dioxide off. If oxidised, it might cause a small amount of lead precipitation; but if much sulphate had been formed, the effect on the p_H value would be so enormous that the sample would be detected as abnormal at once. Dr. Lampitt had mentioned traces of other acids. They had never found them to occur in sufficiently large quantities to disturb the results. In any case, any traces of unusual acids fell into one of the three groups shown.

The Separation and the Determination of Traces of Lead in the Presence of Traces of Bismuth

PART II. ORGANIC COMPOUNDS

BY J. HUBERT HAMENCE, M.SC., A.I.C.

IN a previous paper (ANALYST, 1933, 58, 461) a method for the colorimetric determination of traces of lead in the presence of traces of bismuth was described. This method, however, is not applicable to compounds with organic acid radicles such as tartrates, which would inhibit the precipitation of the ferric hydroxide by ammonia. A slightly modified method has now been devised which is suitable for such compounds, and which may also be employed to determine the lead in phosphates and in the solution obtained after the destruction of organic compounds by wet oxidation, when traces of bismuth are also present.

CO-PRECIPITATION OF LEAD AND FERROUS SULPHIDES.—When hydrogen sulphide is passed through a solution containing ferrous ammonium citrate and traces of a lead salt, made alkaline to a p_H of 8 by the addition of ammonia, the lead is quantitatively precipitated with ferrous sulphide. The colloidal lead sulphide with which we are familiar in the lead test, and which is often so difficult to coagulate, is carried down with the ferrous sulphide.

The mixed sulphides are filtered off, washed, dissolved in dilute nitric acid, and the iron is separated from the lead by the thiocyanate process (Hamence, ANALYST, 1932, 57, 622). The efficacy of this method for the separation and determination of lead was tested in the following manner:

Five grms. of the compound to be tested were dissolved in about 20 ml. of water, 10 mgrms. of crystalline ferrous sulphate and 1 grm. of lead-free citric acid were then added; when solution was complete, ammonia was introduced until the p_H was about 8, two drops of universal indicator being added to the solution in order to ascertain this, and then hydrogen sulphide was passed into the liquid for 15 minutes. The precipitate was filtered off and washed with saturated hydrogen sulphide water made just alkaline with ammonia. This precipitate was dissolved in dilute nitric acid, and the iron was separated by the thiocyanate process.

The following results were obtained with lead-free compounds to which known amounts of lead had been added:

Compound	Lead added Mgrms.	Lead found Mgrms.
Citric acid	0·20	0·20
Rochelle salt ..	0·20	0·21
Sodium acetate ..	0·05	0·06
Sodium phosphate ..	0·15	0·15

SEPARATION OF BISMUTH AND LEAD.—This method of separation by the co-precipitation of the lead as sulphide with ferrous sulphide provides a process by which lead and bismuth may be precipitated from a solution containing organic acid radicles and phosphates; then, having been separated from the large quantities of interfering salts, they may themselves be separated by the pyridine thiocyanate process.

METHOD.—Five or 10 grms. of the compound, 10 mgrms. of ferrous sulphate, and 1 grm. of citric acid, are dissolved in about 25 ml. of water, ammonia is added until the p_H is 8, and hydrogen sulphide is passed into the liquid for 15 minutes. The solution is filtered through a small (No. 31) Whatman paper, and the precipitate is washed well with hydrogen sulphide water made just alkaline with ammonia; it is important that the precipitate should be washed free from citrates. The filter paper and the precipitate are then boiled with 25 ml. of water and 0·6 ml. of concentrated nitric acid. When the sulphides have completely dissolved (which is indicated by the absence of the black sulphide colour) the solution is filtered through the original filter and washed with water. No trouble has been experienced through the separation of sulphur. The filtrate and washings (which should amount to 30 ml.) are then transferred to a separator, and 2 ml. of saturated ammonium thiocyanate solution are added. Pyridine is added until a turbidity is produced, the red thiocyanate colour not being completely bleached (0·9 ml. to 1·0 ml. should be required), and the solution is extracted twice with a mixture of 15 ml. of ether and 15 ml. of amyl alcohol. The aqueous layer is then filtered, the filter-paper being washed once with water and the lead in the filtrate being determined colorimetrically by the sulphide method.

The following results were obtained with 5-grm. portions of different compounds to which known amounts of bismuth and lead had been added:

Compound	Lead added Mgrms.	Bismuth added Mgrms.	Lead found Mgrms.
Rochelle salt ..	0·05	1·0	0·055
Sodium phosphate	0·30	2·0	0·27
Sodium acetate ..	0·10	1·5	0·10
Tartaric acid ..	0·40	0·50	0·38

VISCERA AND ORGANIC COMPOUNDS.—The organic matter is destroyed by the wet oxidation method, nitric acid being added, drop by drop, until the sulphuric acid in the Kjeldahl flask is completely colourless. When all the nitrous fumes have been driven off, the solution is allowed to cool and 20 ml. of water are added; the flask is heated again until white fumes of sulphuric acid are visible. When cold, the contents of the flask are diluted with a small quantity of water and poured into a beaker. The flask is then boiled out twice with 10 ml. of 20 per cent. ammonium acetate solution, and finally washed out with a little water. Two grms. of lead-free citric acid and 10 mgrms. of ferrous sulphate are added to the sulphuric acid solution and washings from the flask, the mixture is heated until any undissolved calcium sulphate has dissolved, and the p_H is adjusted to 8. The process is then continued as described in the previous section. In some cases it may be necessary to add more citric acid in order to dissolve all the calcium phosphate.

The following table shows the results obtained by this process:

Substance		Lead added Mgrms.	Bismuth added Mgrms.	Lead found Mgrms.
Ox-liver, 25 grms.	..	Nil.	Nil.	0·01
Ox-liver, 25 grms.	..	0·05	10·0	0·06
Ox-liver, 25 grms.	..	0·50	0·5	0·45
Ox-kidney, 25 grms.	..	0·40	0·5	0·35
Sardines, 10 grms.	..	—	—	0·07
Sardines, 10 grms.	..	—	5·0	0·065

The lead in the first sardine experiment was determined by a dilute sulphuric acid and alcohol precipitation method, after wet oxidation of the organic matter. Bismuth nitrate was added to another portion, and the lead in the mixture was determined by the method previously described.

Since the publication of the first paper on the separation of lead and bismuth, the method has been tested with larger amounts of bismuth than had been used before. Some of the results obtained are given below:

		Lead added Mgrms.	Bismuth added Mgrms.	Lead found Mgrms.
Calcium chloride, 5 grms.	..	0·25	5·0	0·22
Calcium chloride, 5 grms.	..	0·08	10·0	0·06

Two extractions with the amyl alcohol and ether mixture were made in each case.

When larger quantities of bismuth, such as these, are added, the greater part of the bismuth is precipitated as an insoluble basic bismuth thiocyanate. This remains in the interface between the ethereal layer and the aqueous layer after extraction, and any traces remaining in the aqueous layer are removed when the solution is filtered.

The following results were obtained by treating a solution containing traces of lead and bismuth with ammonium thiocyanate and pyridine, and filtering off the bismuth compound:

To 30 ml. of a neutral solution of lead and bismuth nitrates were added 0·5 ml. of concentrated nitric acid and 2 ml. of saturated ammonium thiocyanate solution. One ml. of pyridine was then added and, after standing for some minutes, the solution was filtered and the precipitate washed once with water. The lead in the filtrate was determined by the sulphide method.

Lead added Mgrms.	Bismuth added Mgrms.	Lead found Mgrms.
Nil.	5·0	Less than 0·01
0·05	5·0	0·05
0·20	5·0	0·19

I wish to thank Dr. A. M. Ward for his helpful advice and criticism during this investigation.

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Notes

The Editor wishes to point out that the pages of the Journal are open for the inclusion of short notes dealing with analytical practice and kindred matters. Such notes are submitted to the Publication Committee in the usual manner.

THE EXTRACTION OF QUININE

In a case recently heard in Birmingham (Analyst, 1934, 174) it was contended that if ether were used for extracting the quinine from a solution of quinine sulphate, the weight of the residue of anhydrous quinine left on evaporation of the extract would be too high after being dried at 100° C., whereas correct results would be obtained if chloroform were used for the extraction.

To test this statement I weighed out two portions of 0·120 grm. each of anhydrous quinine sulphate (obtained by drying the B.P. salt at 100° C. until constant in weight), and dissolved each of these in 50 ml. of slightly acidulated water. One portion was rendered alkaline with ammonia and extracted four times with chloroform, and the other was similarly extracted with ether. The residue from each extraction was dried at 100° C. and weighed, then placed in the steam-oven for another two hours and again weighed. There was no further loss in weight. The actual weight of anhydrous quinine, both from the ether and chloroform extractions, was 0·104 grm.

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THE DETERMINATION OF QUININE

In the report of a case on the dispensing of quinine sulphate given in the Legal Notes of the last issue (Analyst, 1934, 173) it is contended that high results are obtained when quinine is determined by extraction with ether. The residue is stated to contain water which is difficult to drive off at 100° C., but that extraction with chloroform yields anhydrous quinine.

On more than one occasion we have shown that identical results are obtained by extraction of quinine with ether and with chloroform, and that after the residues have been dried at 100° C. no loss in weight occurs on further drying at 125° C. It may also be mentioned that with several preparations the British Pharmacopoeia directs ether to be employed for the extraction of quinine and the residue to be dried at 100° C. In the case of quinine tannate it states "evaporate the mixed ethereal solutions, dry the residue at 100°, and weigh the anhydrous quinine."

In order again to check the point, a re-examination has been made of the sample referred here in connection with the case in question. Chloroform was used to extract the quinine, and the amount found was 0·21 grm. per 100 ml., an identical result with that obtained when ether was used for the extraction.

The alkaloid extracted by ether in the original analysis was checked against a standard sample of quinine by comparing the fluorescences of dilute sulphuric acid solutions under the mercury lamp. The purity of the extracted quinine was thus established.

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NOTE ON THE DETERMINATION OF ALUMINIUM IN NICKEL ALLOYS

In a recent issue of The Analyst (1934, 16), Nickolls has described a method for the separation and determination of aluminium in magnesium alloys.

The aluminium and iron, together with comparatively large amounts of manganese, zinc, or nickel, are separated from the magnesium by the addition of sodium sulphide. From the solution of this precipitate the aluminium, iron, and manganese are precipitated with ammonia, and the nickel and zinc are determined in the filtrate.

For the analysis of nickel alloys containing moderately small amounts of aluminium I have not found this method of separating aluminium from nickel, etc., to be satisfactory.

Blum (*Sci. Papers*, No. 286, Bureau of Standards) has stated that aluminium cannot be satisfactorily separated from nickel, zinc, cobalt and manganese by precipitation with ammonia and ammonium chloride, owing to co-precipitation of the hydroxides of these metals at the p_H value most suitable for aluminium.

Lundell and Knowles (*J. Amer. Chem. Soc.*, 1923, **45**, 676) state that, by following Blum's directions, moderate amounts of manganese and nickel can be separated equally well by precipitation with ammonia and ammonium chloride as by the basic acetate process, but they find that the method breaks down in the case of manganese if phosphorus and vanadium are present, and that the separation of aluminium from zinc, copper, and cobalt is incomplete.

Kling and Lassieur (*Compt. rend.*, 1924, **178**, 1551) found that, in the basic acetate process, aluminium could be precipitated completely at p_H 5·2, zinc and manganese at p_H 6·0 and 6·5, respectively, and that complete separation of aluminium from these elements is possible at p_H 5·2. Although nickel does not precipitate until p_H 6·1 is reached, yet no satisfactory separation from aluminium could be obtained.

In the case of the nickel aluminium alloy mentioned above, the amount of nickel was large compared with that of aluminium. The basic acetate method was found less effective than the ammonia and ammonium chloride separation. With this, a reasonably complete separation of the aluminium could rarely be achieved in less than three precipitations, and the ignited precipitate of alumina was frequently slightly coloured.

The following method has been found to give a satisfactory separation with one precipitation only:—To the cool, weakly acid solution of the nickel alloy, a strong solution of potassium cyanide is added until the precipitate at first formed re-dissolves, to form potassium nickelocyanide, $K_2Ni(CN)_4$. The solution is then poured slowly, and with constant stirring, into an excess of ammonia. The precipitated aluminium hydroxide is allowed to settle and is then filtered off, washed with 2 per cent. ammonium nitrate solution, dried, ignited and weighed. The precipitate obtained in this way is invariably white.

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NOTE ON THE DETERMINATION OF SULPHUR IN ALLOY STEELS

Evolution methods which depend on the solution of a sample of steel in hydrochloric acid and the absorption of the hydrogen sulphide formed in a suitable medium are usually not applicable to alloy steels. Gravimetric methods are generally long and tedious and not suitable for routine tests. A combustion method affords a rapid and convenient means for the determination.

The method described by Holthaus (*Stahl u. Eisen*, **1924**, **44**, 1514) consists in the combustion of the sample in a stream of oxygen, absorption of the oxides of sulphur produced in a measured volume of a standard solution of sodium hydroxide containing hydrogen peroxide, and titration of the excess of alkali with a standard solution of sulphuric acid, sodium alizarin sulphonate being used as indicator.

This method necessitates very rapid combustion of the sample (2 grms. in about 1 minute) at a temperature of about 1200° C. Wear and tear on the combustion tube is, therefore, very considerable, especially as the molten oxide of iron sometimes penetrates through the boat and adheres to the walls of the tube. Considerable spurting of oxide also occurs during the combustion period. In order to minimise the deleterious effects of the oxide, a layer of alundum powder was placed in the combustion zone of the tube and in the bottom of the boat underneath the sample. This procedure certainly increased the life of the tube, but low results were obtained whenever alundum was used in this manner. It was also noticed that when the combustion tube was slightly tilted the boat was frequently perforated by the molten oxide. Maintaining the tube in a horizontal position lessened this effect very considerably. Morgan combustion tubes and boats of a similar composition were found to be fairly resistant to the attack of the molten oxide.

Another difficulty in the Holthaus method is the detection of the end-point. The colour change is very sensitive, and much experience is necessary to obtain consistent results. The weight of sample that can be used in a determination is limited, and this means that the titration must be carried out very carefully. The use of an incandescent lamp screened by means of an opalescent glass plate is recommended by Holthaus for the titration. The use of a lamp of the daylight type (tinted blue) is a decided improvement.

No.	Sample Type	Sulphur	
		Combustion Method Per Cent.	Gravimetric Method Per Cent.
1	Standard Steel ..	0·028	0·027
2	Cr 18, Ni 8, W 1 ..	0·016	0·016
3	,, ..	0·016	0·018
4		0·017	0·015
5		0·020	0·017
6		0·018	0·015
7		0·020	0·021
8		0·021	0·024
9	Cr 1, Mo 0·5	0·033	0·032
10	Cr 18, Ni 8	0·016	0·015
11	,, ...	0·018	0·019
12	,, ...	0·016	0·019

The employment of glass wool as a filter for retaining iron oxide carried over during the combustion requires caution, as glass wool is frequently alkaline and absorbs sulphur dioxide from the gas stream before it reaches the absorption vessel. Iron oxide fume is usually produced when the combustion takes place under pressure, the pressure being due to the smallness of the jet in the absorption vessel. If the size of the jet is so adjusted that very rapid combustion can be obtained without the undue accumulation of pressure in the apparatus, the amount of iron oxide fume produced is negligible, and a glass wool filter is, therefore, not necessary. Also the accumulation of pressure in the apparatus during combustion usually results in low values for the percentage of sulphur.

A temperature of 1150° C. appears to be ample for the combustion of ordinary carbon steels, but for chrome-nickel steels of the 18·8 type a temperature of 1350° C. is necessary. There is no advantage in using too high a temperature. The rate of combustion, however, is very important; the sample should be burnt as rapidly as possible.

The results of sulphur determinations on a number of steels by the combustion method and by a gravimetric method are given in the subjoined table. Some experience and considerable care are required in order to realise, in practice, the accuracy claimed for this method.

I wish to thank Messrs. Stapleton, King and Jenkins who carried out the experimental work.

T. E. ROONEY

THE NATIONAL PHYSICAL LABORATORY
TEDDINGTON, MIDDLESEX

Department of Scientific and Industrial Research

THE INVESTIGATION OF ATMOSPHERIC POLLUTION

REPORT AND OBSERVATIONS IN THE YEAR ENDING MARCH 31, 1933*

THE present publication is the 19th of the series, and consists of the Report of the Standing Conference to the Co-operative Bodies for the Year 1932 to 1933, p. 1–3; the Report of the Atmospheric Pollution Research Committee for the year, p. 4–7; the Report of the Superintendent of Observations, p. 8–45; Appendices I and II; and the General Deposit Tables, p. 51–99.

SULPHUR GASES IN AIR.—Regular observations of sulphur dioxide concentration by the "lead peroxide" method, developed by the Building Research Station of the Department (ANALYST, 1933, **58**, 284), have been extended to 22 stations, and the close correspondence of readings obtained with 2 cylinders placed close together shows the reliability of the procedure. The method is still in the experimental stage, but seems likely to be a valuable supplement to the volumetric method.

PHOTO-ELECTRIC METHOD OF MEASURING OPTICAL INTENSITY OF SMOKE ISSUING FROM A CHIMNEY.—Existing methods of estimating smoke pollution are based on eye observations only, or eye observations aided by the Ringelmann chart or a similar standard of comparison. An apparatus is now being developed which uses a photo-electric cell so arranged as to measure the amount of light received from a definite area of the smoke, as compared with that from an equal area of sky. The light from the smoke consists of both transmitted and reflected light, and this modifies the direct relationship between measured "optical density" and pollution in the case of dense smokes. To minimise the errors likely to arise from the reflected light, which varies with different types of smoke and under different conditions of illumination, an ultra-violet filter may be used with the apparatus, but, even so, it is necessary to determine the general form of the relation between apparent brightness of the smoke and the amount of pollution. Further, allowance should be made for the effect of light scattered by the air between the smoke and the instrument by making observations not only on the sky and the smoke trail, but also on the tops of the chimneys. During the preliminary work with the apparatus the smoke under observation was classified by eye into one of the six classes: very light, light, light medium, medium, medium excessive, and excessive, and analysis of the readings recorded showed that there is a well-defined reading for each class of smoke, so that the instrument may be used to determine when the chimney smoke is of a greater density than the prescribed limit. It is hoped soon to be able to make the instrument the basis of rough measurements of the relative total amounts of pollution emitted by the chimney in a given period.

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* Published 15th February, 1934, pp. 99. Obtainable at Adastral House, Kingsway, W.C.2. Price 5s. net.

JET DUST COUNTER.—It is now established that this apparatus provides a satisfactory measure of the number of insoluble particles usually present in the air.

DAYLIGHT MEASUREMENT.—Daylight estimations by the potassium iodide method have been made throughout the year at two stations at Halifax, and it was found that the more heavily polluted of the two stations lost, in 1931 to 1932, as much as 20 per cent. of sunlight as recorded by the amount of iodine liberated, and in 1932 to 1933, 17 per cent., the proportionate loss being much greater in winter than summer. The corresponding figures for deposited impurity at the two stations were for 1931 to 1932, 281 and 133 tons per sq. mile, respectively, and for 1932 to 1933, 297 and 121 tons. A similar series of figures was obtained at Salford, but more figures are needed for other places.

RECORD OF OBSERVATIONS.—The total number of deposit gauges in use throughout the year was 91, together with 3 automatic filters. The maximum and minimum monthly deposits, as metric tons per sq. km. (conversion tables are given, and the figures also tabulated as English units) were: *Tar:* London (South Kensington), 147; Salford (Ladywell Sanatorium), 19; *Other insoluble carbonaceous matter:* Edinburgh, (Princes Street), 130; Marple, 32; *Insoluble ash:* Edinburgh (Princes Street), 145; Salford (Ladywell Sanatorium), 62; *Ash of soluble matter:* London (Ravenscourt Park), 154; Rochdale (Town Hall), 58; *Total solids:* Birmingham (West Heath), 144; Marple, 64; *Rainfall:* Leicester (Western Park), 129; Rochdale (Town Hall), 75. The recorded figures show that although, on the whole, improvement has continued, in that there was a decrease of 11 per cent. in the average total solids, this improvement has not been so great as in the last 2 years (20 and 24 per cent., respectively). Sulphate deposits have markedly decreased during the year, but the increase during the last 2 years at Ravenscourt Park has again been maintained. Attention is called to the unique distribution of suspended impurity at Cardiff, where some unusually heavy output occurs about 2 or 3 p.m. Cardiff is also remarkably free from sulphur pollution, and throughout the year there was not a single observation with over 0·2 part per million.

APPENDIX I deals with the sunlight and ultra-violet light measurements at Salford, and gives a description of Dr. Ashworth's method (ANALYST, 1933, **58**, 690).

APPENDIX II discusses atmospheric corrosion as related to atmospheric pollution. The effects of minute quantities of polluting substances on metals are sometimes represented by preponderating amounts of sulphates or basic sulphates in the final products. Thus, the green patina on copper after prolonged exposure to the air has been shown to consist essentially of basic copper sulphate, not basic copper carbonate, as it was previously assumed to be. Any effect due to large amounts of carbon dioxide has been shown to be quite undetectable in the presence of excessively smaller concentrations of sulphur dioxide.

D. G. H.

REPORT OF THE WATER POLLUTION RESEARCH BOARD

For the Year Ended 30th June, 1933*

This is the Sixth Annual Report of the proceedings of the Water Pollution Board, and there is an accompanying Report of the Director of Water Pollution Research (Dr. H. T. Calvert).

Water-Borne Disease.—The need for even greater vigilance than in recent years is occasionally emphasised by outbreaks of water-borne disease, such as the outbreaks of enteric fever at Malton and at Denby Dale, in 1932, and the outbreak of paratyphoid in Epping during 1931. Part of the Epping sewage effluent discharges into Cobbin's Brook, which enters the River Lea above the Metropolitan Water Board's intake from that river. Samples of the sewage effluent still contained paratyphoid bacilli at the end of June, 1933. Disinfection of Cobbin's Brook by means of chlorine was begun in February, 1931, and has since been continued. After chlorination the water does not contain *B. coli* in 100 ml., or paratyphoid bacilli in 500 ml. In addition the filtered water from the waterworks has been disinfected by treatment with ammonia and chlorine, and for a short period the River Lea was not used for the supply.

Beet Sugar Effluents.—The investigations described in the last Annual Report (Analyst, 1933, **58**, 282) have been continued. Several hundred strains of bacteria were isolated from the percolating filters at the factory at Colwick, and have now been examined in Rothamsted Laboratories. From the results of the examination it appears, that, in general, those species of bacteria most active with carbohydrates also most readily attack the salts of organic acids. In experiments on the effect of adding phosphate to solutions of sucrose prior to treatment on the percolating filters, it was found that active biological films were deposited on the filtering media, and that under certain conditions the biochemical oxygen demand of the treated effluent was less than 2 per cent. of that of the original solution.

Milk Factory Effluents.—Experiments at Rothamsted have shown that milk diluted with water to contain 1·3 per cent. of milk can be readily oxidised biologically by filtration through gravel at the rate of 100 galls. per day per cb. yard of filtering medium. To prevent clogging of the filters, the effluent must be treated in two stages (*cf.* Richards and Cutler, *Water Pollution Research Technical Paper*, No. 3, 1933).

Biological Oxidation of Cellulose.—Experiments showed that aqueous suspensions of cellulose in the form of wood pulp are hardly oxidised by the activated sludge process, but with percolating filters about 70 per cent. of the cellulose is oxidised in a suspension of 50 parts per 100,000 by filtration at the rate of 100 galls. per day per cb. yard of filtering material.

Survey of the River Tees.—The comprehensive scientific survey of the River Tees has been completed, and will shortly be published in a final report. The factors influencing the self-purification of the river from *sewage* pollution have been systematically studied. Of these factors, temperature is the most important, the rate of self-purification increasing rapidly as the temperature is raised from 10° to 20° C. A survey of the comparatively unpolluted Estuary of the River Tay has been made, and the results have been compared with those for the River Tees.

Methylene Blue Test for Stability of Sewage.—As a result of the various experiments the following method of testing a sewage or sewage effluent with methylene blue has been proposed. Two Thunberg tubes are each supplied with

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* H.M. Stationery Office, Kingsway, London, W.C.2. 1934. Price 1s. net.

the same quantities of a washed sewage sludge, a hydrogen donator such as formate, 1 ml. of a 0·02 per cent. solution of methylene blue, and buffer solution of a p_H value of 7·4. To one of the tubes, 3 or 4 ml. of the sewage to be examined are added, and a similar volume of water is added to the second tube to serve as a control. The tubes are then evacuated and incubated at 45° C. In the control the methylene blue is usually decolorised in less than an hour. If the sample under examination in the other tube is crude domestic sewage, the time required for reduction of the methylene blue is usually rather less than with the control, whereas it is much greater with samples of a well-purified sewage effluent. Examples of the results obtained with crude sewage and treated sewage from three purification works are given in tables.

BASE-EXCHANGE PROCESS OF WATER SOFTENING.—A new type of apparatus has been devised for examining the softening powers of various base-exchange materials for water containing varying amounts of different salts of calcium and magnesium.

PLUMBO-SOLVENT WATERS.—The summary of existing knowledge on this subject has been revised and enlarged and is to be published as *Water Pollution Research Technical Paper*, No. 4. Preliminary experiments on the possibility of contamination of water by lead through the leakage of electric current through service pipes have indicated that, unless the leakage of current is exceptionally large, appreciable increase in the quantity of lead in the water is unlikely.

COLLOIDS OF SEWAGE AND BEET SUGAR EFFLUENTS.—An account is given of the further investigations carried out at University College, London, under the direction of Professor Donnan. Samples of sewage from the Birmingham area and of effluent from the beet sugar factory at Colwick have been examined by ultra-filtration, gravity sedimentation and centrifuging at different speeds. A beginning has also been made in a study of the electrical properties of sewage colloids.

Hong-Kong

REPORT OF THE GOVERNMENT ANALYST FOR THE YEAR 1932

MR. V. C. BRANSON, the Government Analyst, refers in his report to the great loss suffered by the Department by the death of his predecessor, Mr. E. R. Dovey.

The number of analyses made during the year was 2706, as compared with 2720 in 1931.

FORENSIC CHEMISTRY.—Of the 146 examinations made, 115 were in connection with toxicological work, arising out of 91 cases. No poison was found in 54 cases, opium was found in 21, adalin in 3, alcohol in 2, lysol in 2, veronal in 2, barbituric acid in 2, and potassium cyanide, hydrochloric acid, morphine, formaldehyde and mercury in 1 case each.

Poisonous Sweets.—Several children showed symptoms of poisoning after eating sweetmeats made locally. It was ascertained that an excess of synthetic essences had been used, and that the wrapping paper contained aniline dyestuffs which had contaminated the sweets.

FOOD AND DRUGS.—Of the 268 samples examined, 56 consisted of milk, 27 of bread, 13 of butter, and 6 of tea. The only samples found to be adulterated were 3 of milk and 1 of tea, which contained exhausted leaves. There is no doubt that the number of samples normally submitted for examination is very much too low, considering the population of the Colony. The reason for the low figures is due, possibly, to the state of the Regulations covering the sale of Food and Drugs. There is at present only one standard for foodstuffs laid down, *i.e.* that for fresh milk. Draft definitions or standards for the most important foodstuffs were submitted by the late Mr. E. R. Dovey in August, 1927, and embodied in a new Food and Drug Bill printed in November, 1930. Until this Bill becomes law, the present unsatisfactory state of affairs will remain.

COLOURING OF PETROL.—At the end of the year an investigation was carried out for the Roads Department, to ascertain whether it would be possible to colour petrol, issued to Government lorries, so that unauthorised use of this petrol could be detected. The best concentration of a suitable dye was found, and a trial is to be made during the early part of 1933.

United States Pharmacopoeia Vitamin Standards*

THERE being only a limited amount of the International Vitamin *A* and *D* Standards available, the U.S.P. Vitamin Advisory Board undertook the preparation of a sufficient quantity of a cod-liver oil of known vitamin potency to be used as the basis for the standardisation of American medicines and foods claiming "A" or "D" vitamin potency. The Vitamin Board secured the co-operation of the Bureau of Fisheries at Washington—who supplied a sufficient quantity of authentic cod-liver oil collected and de-stearinated under the supervision of the Government Laboratory in Gloucester, Massachusetts. This oil was immediately placed in 30-ml. amber-colour glass containers under rigid conditions involving the drying of the container and oil, the exclusion of all air by the use of a vacuum, the introduction of carbon dioxide, and hermetic sealing of the containers. The containers of oil were placed immediately in cold storage below 15° C. The Board then arranged with seventeen vitamin laboratories to assay this bottled oil, following exactly the assay methods adopted by the large vitamin committee. All laboratories reported only by code number, the Chairman of the Board alone holding the key.

Fifteen of the seventeen laboratories have already reported, and the other two have the assays in hand. The Vitamin Board has painstakingly studied and evaluated the reports and has recommended the following standards for the official cod-liver oil:—

Minimum Standard for Vitamin A for U.S.P. Cod-liver Oil.—The minimum Vitamin *A* standard for U.S.P. Cod-liver Oil shall be not less than 600 International Units.

Minimum Standard for Vitamin D for U.S.P. Cod-liver Oil.—The minimum Vitamin *D* standard for U.S.P. Cod-liver oil shall be not less than 85 International Units.

Note.—The new "U.S.P. Vitamin Units" and "U.S.P. Vitamin D Units" are identical with the corresponding "International Units." In expressing on labels the potency of vitamin-containing products, it is recommended that the term "U.S.P. Vitamin *A* Units" or "U.S.P. Vitamin *D* Units" be employed. To indicate the adoption of the *new* standards the statement "U.S.P. X—Revised 1934" may be used.

RELATIONSHIP OF VITAMIN UNITS.—For the benefit of manufacturers or others who wish to know the approximate relationship between units they are now using and International Units of vitamins *A* and *D*, the following information is provided:—

One U.S.P. X Sherman or A.D.M.A. unit of vitamin *A* equals 1·4 International or new U.S.P. Units.

One Steenbock Unit of vitamin *D* equals 2·7 International or new U.S.P. units.

One International or U.S.P. unit of Vitamin *D* equals 3·25 A.D.M.A. units.

The U.S.P. Board of Trustees has also announced the release of the "Reference Cod-liver Oil," prepared under the supervision of the Vitamin Board, for use in the standardisation of medicinal or food products claiming vitamin potency, and already many laboratories in the United States have secured this official vitamin standard. These new U.S.P. Standards of vitamins *A* and *D* will be the basis for the evaluation by the Food and Drug Administration of all products in U.S.A. claiming vitamin *A* or *D* potency.

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* *Amer. J. Pharm.*, 1933, 105, 583–587.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs Analysis

Colouring Matter in American Red and Purple Tomatoes. M. B. Matlack and C. E. Sando. (*J. Biol. Chem.*, 1934, **104**, 407–414.)—Previous work by various investigators on the red pigment "lycopene" of the tomato (*Lycopersicum esculentum*) is briefly summarised. Most of the work was carried out on the pigment from Italian-grown varieties. These tomatoes are smooth, plum-shaped, approximately three inches long and one inch in diameter, have firm flesh and practically no core, and usually have a more brilliant and more uniformly distributed red colour than the average tomato grown in the United States. American-grown tomatoes are large and globular, and generally more juicy. In America, two distinct types of red tomatoes are recognised. One type is carmine-red with a purplish cast. Tomatoes of this type are characterised by purplish-red flesh and transparent skin, and are sometimes described as purple tomatoes. Typical examples are Livingston Globe and Cooper Special. In the second type the colour approaches scarlet-red. These tomatoes are characterised by purplish-red flesh and yellow pigmented skin, which points together cause the colour to appear more nearly true red. The Stone, Indiana Baltimore and Santa Clara Canner are examples of this type. It was decided to isolate and study the pigment from American red and purple tomatoes, and to determine whether it is identical with that isolated from Italian varieties. The results of such an investigation would definitely answer the question often raised by canners as to whether the pigments are the same in American red and purple varieties. Four varieties of tomatoes were used, namely Fiaschetti (Italian-grown red), Indiana Baltimore (American-grown red), Santa Clara Canner (American-grown red) and Cooper Special (American-grown purple). The method employed for the isolation of the crude pigment was essentially that of Willstätter and Escher (*Z. physiol. Chem.*, 1910, **64**, 47). It was found that the pigment obtained from the American-grown red and purple varieties was identical with lycopene isolated from the Italian variety (Fiaschetti). P. H. P.

Further Observations on Factors which influence the Component Fatty Acids of Butter. H. K. Dean and T. P. Hilditch. (*Biochem. J.*, 1933, **27**, 889–897, *cf.* ANALYST, 1930, **55**, 702.)—Further work has now been carried out on the butter-fats from milks of various cows (in many cases the same cows as were used previously) belonging to the typical herd of the National Institute for Research in Dairying, Shinfield. The samples represented the period 1928 to 1932, and the data now presented, taken in conjunction with the earlier work, afford means for detecting two characteristic changes in the composition of the fatty acids. The first is the seasonal change occurring when the cows return to pasture; and the second, which appears to be a function of the age of the cow, consists in a gradual augmentation in the proportion of unsaturated components of the fat. The facts that the analyses cover four seasons, and are concerned chiefly with the same cows throughout, enable safe conclusions to be drawn. The seasonal change consists in an abrupt and relatively immediate increase in the proportion of oleic and linolenic acids, with a simultaneous decrease shared almost wholly by the butyric and stearic acids. The same change has been observed in each of the four seasons involved, and the increase in unsaturated acids amounts to 4 per cent. (mols.) and takes place within 2 to 3 weeks, or even less, after the cows are put out to grass. In addition to the abrupt seasonal rise in iodine values, there is a definite tendency for the iodine values of the pasture milk fats to rise throughout the series, and this increase is probably a function of the age of the cow. Whilst the Reichert-Meissl values tend to vary inversely with the iodine values, the alteration is not so regular or abrupt. In studying the gradual augmentation of C_{18} acids, in the progressive analyses of milk fat from a given cow with the corresponding diminution of palmitic acids, seasonal factors were eliminated, so far as possible, the comparison being based on the fats from pasture-fed animals of the seasons 1928 to 1932, and the conclusion is arrived at that the increase corresponds with the increasing age of the cow. It is suggested that a similar range of variation observed by Banks and Hilditch (ANALYST, 1931, **56**, 816) for beef-tallows may be connected in the same way. D. G. H.

Body Fats of the Pig. III. Influence of Body Temperature on the Composition of Depôt Fats. H. K. Dean and T. P. Hilditch. (*Biochem. J.*, 1933, **27**, 1950–1956.)—In order to ascertain whether the respective layers of fat in the pig on either side of the "streak" are homogeneous, or whether there is a progressive alteration as the skin is approached, the central portion of the whole of the back fatty tissue from a very fat sow was divided into five layers of approximately equal thickness, two from the "outer" portion between skin and streak, and three from the inner portion beneath the "streak." The fat was extracted by means of acetone, and the component acids present were determined as in previous studies (ANALYST, 1932, **57**, 531). Unsaturated acids of lower molecular weight than oleic acid were specially looked for in the fat of the Inner III sample, but, if present, they were estimated to be less than 1 per cent. of the total fatty acids. The molar distribution of the individual acids was as follows:

Fat	Myristic	Palmitic	Stearic	Oleic	Linolic	C_{20-22} unsaturated
Outer I ..	3·1	25·6	9·8	45·0	14·8	1·7
Outer II ..	3·4	25·1	12·6	41·8	15·3	1·8
Inner I ..	3·5	26·6	14·0	41·4	13·6	0·9
Inner II ..	3·3	27·2	14·0	40·1	14·2	1·2
Inner III ..	3·6	26·2	14·0	41·6	13·4	1·2

The component acids of the three "inner" layers were thus almost identical, but the outermost contained slightly less palmitic and about 4 per cent. less stearic, and correspondingly more oleic acid. The detailed analytical figures confirm the conclusion of Henriques and Hansen (*Skand. Arch. Physiol.*, 1901, **11**, 151), that there is a close relationship between increase in saturation of the fat and increasing body-temperature. At the same time the greater part of the fat beneath the streak was evidently completely homogeneous. The high proportion of linolic acid and of 1 to 2 per cent. of highly unsaturated acids of the C_{20} and C_{22} series is probably characteristic of pigs of considerable age, and not due to the diet (maize meal, thirds and whey). The statement that warm-blooded animals and plants of tropical origin produce more solid saturated fats than cold-blooded animals or plants from cooler regions, is shown to be only partly true. D. G. H.

Kernel Fats of Some Members of the Palmae. G. Collin. (*Biochem. J.*, 1933, **27**, 1366–1372.)—A quantitative estimation of the component fatty acids has been made for five more kernel fats of the *Palmae* order. In the case of *Acrocomia sclerocarpa* Mart, *Manicaria saccifera*, Gaertn, and *Astrocaryum Tucuma* Mart, the quantity of fat available was sufficient for the attainment of the normal standard of accuracy; for *Maximiliana caribaea* Griseb, and *Attalea excelsa* Mart, only a rough estimation of the component fatty acids was possible. In the first case a single fractionation only was possible, the general composition being deduced from the analytical constants of the primary fractions, and in the second case the primary fractionation was so controlled as to correspond closely in size of fraction and range of boiling-point with an average primary fractionation of a Palmae kernel fat, and, by comparison, a general idea of the composition was obtained. The methods of Collin and Hilditch (*J. Soc. Chem. Ind.*, 1928, **47**, 261T; ANALYST, 1929, **54**, 243; 1930, **55**, 291) were followed, except that special precaution was taken to guard against loss of low b.pt. esters during the vacuum distillation. In each case the general composition of the fatty acid mixture followed the usual arrangement found in the kernel-fats of this order.

	Acrocomia sclerocarpa Gru-gru	*Manicaria saccifera*	*Astrocaryum tucuma*	*Maximiliana caribaea* (immature nuts)	*Attalea excelsa*	*Coconut* refined (commercial sample)
Kernel, per cent. of nut	26·0	15·0	—	59·0	3·0	—
Kernel fat, per cent.	44·4	57·7	39·8	48·0	62·6	—
M.pt. of fat	24·0° C.	27·1° C.	30·3° C.	—	25·5° C.	—
Saponification equivalent	222·3	221·8	218·9	236·8	231·7	217·2
Iodine value	17·1	10·7	15·8	22·7	18·2	9·7
Unsaponifiable matter, per cent.	0·45	0·05	0·4	0·23	—	—
Acid value	0·6	0·6	1·8	20·2	—	0·3
Fully-saturated glycerides, per cent.	69·0	82·0	73·0	—	—	—
Mono-unsaturated di-saturated, per cent. mols.	21·0	11·0	18·0	—	—	—
Di-unsaturated mono-saturated, per cent. mols.	10·0	7·0	9·0	—	—	—
Caprylic acid, per cent.	11·5	7·8	1·9	—	broadly as	11·2
Capric acid ,,	6·9	8·0	5·6	6·0	*Acrocomia*	9·2
Lauric acid ,,	47·6	49·9	53·1	50·0	*sclerocarpa*	46·5
Myristic acid ,,	12·2	17·4	20·6	21·0	„	16·5
Palmitic acid ,,	6·3	6·7	5·5	8·0	„	7·7
Stearic acid ,,	1·8	1·8	1·3	?	„	1·8
Oleic acid	12·5	7·3	10·1	15	„	6·0
Linolic	1·2	1·1	1·9		„	1·1
Association ratio	·29 to 1	1·16 to 1	1·25 to 1	—	—	1·3 to 1·4 to 1

D. G. H.

Unsaturated Acid in the Kernel Fat of "Akarittom" (*Parinarium laurinum.*) II. M. Tsujimoto and H. Koyanagi. (*J. Soc. Chem. Ind. Japan*, 1934, **36**, 673–675.)—A further study has been made of the acid isolated from akarittom fat (ANALYST, 1933, **58**, 351) and supposed to be an isomer of elaeostearic

acid. The fat obtained on this occasion had an iodine value (Wijs) of 193·6, as compared with the previously obtained value of 214·1. The new acid was prepared from the fat as before, and, when further refined, melted at 85–86° C. The chief product of decomposition on treating the acid by the ozone method was azelaic acid, with probably some azelaic semi-aldehyde. Oxidation by the permanganate method also yielded azelaic acid with an indication of sebacic acid, judging by the higher m.pt. of the latter fractions. It is now considered possible that the acid is identical with couepic acid, and the previously assigned provisional constitutional formula is withdrawn.
D. G. H.

Fatty Oil of *Parinarium Macrophyllum* (Neou Oil). A. Steger and J. Van Loon. (*Rec. Trav. Chim. Pays-Bas.*, 1934, 53, 197–204.)—The edible nuts of *Parinarium macrophylla* (N.O. *Rosaceae*) of average weight 14 grms., consisted of 91 per cent. of shell and 9 per cent. of kernel, the latter yielding, on extraction with petroleum spirit, 65·2 per cent. of a colourless, pleasant-smelling oil possessing the following characteristics: Sp. gr. at 78° /4°C., 0·8901; n_D^{70}, 1·4741; saponification value, 190·0; iodine value (Wijs) about 162; thiocyanogen value, 78·2; Reichert-Meissl value, 0·33; acid value 0·25; unsaponifiable matter 0·9 per cent.; saturated fatty acids (Bertram) 10·3 per cent.; unsaturated fatty acids 83·8 per cent.; glycerol (as C_3H_2) 4·3 per cent.; and volatile matter 1·6 per cent. The total fatty acids (94·1 per cent., of the oil) showed n_D^{70} 1·4651; a true iodine value of 169·3; acid value 200·2; and mean molecular weight 280·2. The true iodine value of the oil cannot be found by the usual Wijs procedure, and the oil somewhat resembles tung oil and oiticica oil in this respect. Complete saturation with halogen takes a long time, and unsaturation cannot be determined by hydrogenation, since the more unsaturated acids undergo slight polymerisation very rapidly, and this lowers the power of taking up hydrogen. The unsaturation of the oil, as expressed by the iodine value over a period of 168 hours, is 162·3 and partial unsaturation (by means of thiocyanogen solution) is taken as 134. The unsaturated fatty acids were examined by re-crystallisation, bromination, separation by Twitchell's method, elaidinisation, ozonisation, and oxidation with alkaline permanganate solution. The percentage composition of the oil is worked out as:—fatty acids 94·1 per cent., consisting of saturated acids 10·3, elaeostearic 30; linolic 32; and oleic acid 21; unsaponifiable matter, 0·9; glycerol 4·3; and volatile constituents 1·7.
D. G. H.

Oil of "Karasumi." M. Tsujimoto. (*J. Soc. Chem. Ind. Japan*, 1934, 36, 676B.)—"Karasumi" is the salted and dried ovary of the grey mullet (*Mugil japonicus*), and a sample of the orange-yellow, flat, elliptical substance from Formosa yielded, on extraction with ether, about 32 per cent. of a brownish oil, which deposited an appreciable amount of solid at ordinary temperature, and had the following characteristics:—Sp.gr. at 20°/4° C., 0·8818; n_D^{20}, 1·4695; saponification value, 120·1; iodine value (Wijs), 130·6; unsaponifiable matter, 40·64 per cent.; and acid value, 16·0. The fatty acids were semi-solid at 20° C., and had m.pt. 25° to 26° C.; neutralisation value, 196·0; and iodine value, 186·1. They yielded 52·3 per cent. of ether-insoluble bromide, containing 70·09 per cent. of bromine. The unsaponifiable matter was bright orange-yellow, rather hard and crystalline, and contained 9·62 per cent. of cholesterol, as determined by the digitonin method. Fractional distillation of the acetyl derivatives showed that the solid part consisted, besides cholesterol, mainly of cetyl alcohol with a small proportion of octadecyl alcohol. The liquid part consisted of octadecenol, (possibly oleyl alcohol), and hexadecenol also appeared to be present. Karasumi oil is, therefore, to be regarded as a liquid wax, resembling sperm oil and inguandarame oils, except in the higher unsaturation of the fatty acids and the large content of cholesterol. The occurrence in appreciable quantity of cetyl alcohol and octadecenol in the reproductive organs of fish is noteworthy. D. G. H.

Methods for the Determination of Lead in Foods. H. J. Wichmann and others. (*J. Assoc. Off. Agric. Chem.*, 1934, 17, 108–135.)—In this paper six methods are described in considerable detail for the determination of small quantities of lead, with particular reference to spray residues present on fruit, such as apples and pears. The methods, which are adaptations of existing processes, involve the following steps: (*a*) *Preparation of sample*:—Wet oxidation of the whole sample (A.O.A.C., *Methods of Analysis*, 1930, 306), or ashing at a temperature not greater than 500° C., or removal of the spray residue by solvents is employed. The solvent treatment is as follows:—The stem and sepals of the weighed fruit are removed by cutting, and are placed in a funnel inserted in a flask. The fruit is impaled on a glass rod, and immersed in a boiling mixture of 25 ml. of 30 per cent. sodium hydroxide solution, 25 ml. of 10 per cent. sodium oleate solution and 200 ml. of water (which is sufficient for treating a sample lot of 10 fruits) until the skin begins to "check"; it is then removed to the funnel, and rinsed with a stream of hot dilute nitric acid (1 + 49), particular attention being paid to washing out the stem and calyx ends. The alkaline solution is cooled and mixed with the acid solution in the flask. It is claimed that in this way 95 per cent., or more, of the lead is removed "even with the most refractory fruit." (*b*) *Preliminary separation of lead*:—This is either dispensed with, or precipitation as sulphide (*cf.* Fairhall, *J. Ind. Hyg.*, 1922, 4, 9), or sulphate, or extraction of the lead salt of diphenylthiocarbazone (*cf. inter alios* Allport and Skrimshire, ANALYST, 1932, 57, 440), is employed. (*c*) *Determination*:—The methods include precipitation as chromate and titration of the chromate ion (*cf.* Fairhall, *loc. cit.*), anodic deposition of lead peroxide, and iodimetric determination of this (Jones, ANALYST, 1933, 58, 11), colorimetric determination as sulphide (Hamence, ANALYST, 1932, 57, 622), and colorimetric determination with diphenylthiocarbazone (Fischer, *Z. anal. Chem.*, 1933, 46, 442). S. G. C.

Derris Roots from New Guinea. (*Bull. Imp. Inst.*, 1933, 31, 469.)—Samples of fine and coarse roots have been tested for their content of rotenone by a method (recently published by the United States Department of Agriculture) which depends on extraction with carbon tetrachloride. Fine roots from New Guinea contained 3·2 per cent., coarse roots 2·1, and a commercial sample of Malay roots 2·2 per cent. The rotenone-content varies considerably, both with the species and with the age of the plant from which the roots are obtained. A number of commercial samples of derris root, examined by the carbon tetrachloride method, have been found to contain from nil to 6·9 per cent. of rotenone (*cf.* ANALYST, 1932, 57, 782). R. F. I.

Biochemical

Presence of Oxalates in Plants from the Point of View of Oxaluria. A. Goudswaard. (*Pharm. Weekblad*, 1934, **71**, 114–118.)—It has been stated that, with a few exceptions (*e.g.* mushrooms), oxalic acid does not occur in plants in the free state, but it is of greater importance, from the point of view of the study of oxaluria, to know whether oxalates are present in plants in the soluble or insoluble state. Calcium oxalate crystals are not dissolved by 0·4 *N* hydrochloric acid (although soluble in higher concentrations of acid), and this corresponds with an acidity greater than that existing in the stomach. The solubility of oxalates from cooked foods will also depend on the method of cooking; thus, for instance, addition of alkali (*e.g.* to rhubarb or sorrel) increases the solubility by formation of the sodium salt, which is stated to be more harmful (*cf.* Molisch, *Mikrochemie der Pflanzen*). The Table below gives the total oxalate-content, determined by the author's modification of the Van Itallie-Lemke method (*vide infra*), and the soluble oxalate-content per kilo of raw material (+ indicates present, and 0 absent).

Material	Total oxalate-content (French results) per kilo. mgrms.	Total oxalate-content (German results) per kilo. mgrms.	Soluble oxalates by author's method per kilo. mgrms.	Calcium oxalate	Soluble calcium salts
Potatoes	—	400	0		—
Endive	+	100	0	+	+
Beans	310	300	0		+
Chocolate	900	900	—		
Cabbage	+	—	0		
Purslane	—	—	6000 to 7500	+	—
Red beet	390	400	1800	+	—
Spinach	1910 to 3300	3300	Doubtful trace		
Celery	+	+	0	+	+
Tea	3750	3700	Large quantity		
Coffee	120	100	—		
Tomatoes	+	5	0	—	—
Strawberries	—	60	0		+
Plums	120	120	—		
Rhubarb	2460	2400	6440		
Onions	—	—	0	—	—
Carrots	+	—	0	—	+
Sorrel	2740 to 3600	3600	—		
Leeks	—	—	0	+	+
Asparagus	+	—	—		
Pepper	3250	—	—		
Amarantus spec.	—	—	3900	+	—

For comparison, results obtained by French and German chemists are also given.* In the author's method the finely-minced sample (50 grms.) is boiled for 10 minutes with 150 ml. of water, and the mixture is filtered. The filtrate is not decolorised, but to one portion is added calcium chloride solution, and the non-occurrence of a precipitate after 24 hours is taken to indicate the absence of oxalic acid. If any precipitate is produced, it is removed in the centrifuge, washed, and identified microscopically. Ammonium oxalate solution is added to another portion, and, if no precipitate is formed, the absence of calcium salts is indicated; any precipitate is examined as described above, the crystals being then converted into the characteristic crystals of calcium sulphate by means of sulphuric acid. Soluble oxalates are determined by diluting the clear, cold filtrate from an extract of 10 grms. of sample in 150 ml. of hot water (*cf. supra*) to 250 ml., and neutralising 5 ml. of the dilute solution with 0·1 *N* hydrochloric acid, with neutral red as indicator; if a precipitate results, a fresh extract is made, and this is acidified, diluted to 250 ml., and filtered. The filtrate (5 ml.) is treated with calcium chloride, and any resulting precipitate is separated, washed in the centrifuge, and titrated with a 0·01 *N* solution of potassium permanganate (by Kolthoff's method). J. G.

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* No references to the original papers are given.

Isolation of Heteroxanthine from Yeast. P. W. Wiardi and B. C. P. Jansen. (*Rec. Trav. Chim. Pay-Bas*, 1934, **34**, 205–208.)—Brewer's yeast was digested with water containing 0·1 per cent. of benzoic acid, with the addition of hydrochloric acid to give a p_H value of 4·5, and 100 litres of extract were obtained from 40 kilos of yeast. To this extract were added 6 kilos. of fuller's earth, followed, after separation had occurred, by baryta and ice. To the alkaline filtrate, acidified with hydrochloric acid to give a p_H value of 4·8, a solution of sodium silicotungstate (p_H 4·8) was then added until precipitation was complete. The precipitate, when decomposed with baryta in the presence of ice, gave an alkaline solution, and this was acidified with nitric acid to give a p_H value of 2 and then treated with an excess of silver nitrate. The resulting precipitate, containing no vitamin *B*, was decomposed with hydrochloric acid, the solution was filtered and evaporated to dryness, and the residue was extracted with dilute sulphuric acid. By repeating the silver nitrate purification, together with concentration and re-crystallisation from 0·5 *N* hydrochloric acid, 1·2 grm. of a pale yellow crystalline mass was obtained. A consideration of the behaviour of this substance on heating in a tube, and with sodium; the positive murexide, and negative xanthine test; the absence of precipitate with picric acid or sodium picrate, together with a determination of the nitrogen-content, indicated that the substance was a mono-methylxanthine. Further reactions showed that it was heteroxanthine, *i.e.* 7-methylxanthine. Three-quarters of the nitrogen present was in the form of a volatile ammonium base, and one-quarter as amino acid, and the methyl group was shown to be present in the amino acid. The general reactions closely resembled those of heteroxanthine prepared from theobromine. If lead acetate and silicotungstic acid were used in the preparation before addition of fuller's earth, adenine hydrochloride, not heteroxanthine, was eventually isolated. D. G. H.

Isolation and Detection of Bilirubin. C. E. May, R. Martindale and W. F. Boyd. (*J. Biol. Chem.*, 1934, **104**, 255–257.)—The authors have been working over a prolonged period on the isolation and detection of small amounts of bilirubin. Recently, Daddi (*Riv. clin. med.*, **32**, No. 2; *Pathologica*, 1933, **25**, 215) and Laemmer and Beck (*Compt. rend.*, 1933, **113**, 166) reported work along similar lines, and the authors decided to publish the results they had obtained. They state that many substances were tried as bilirubin precipitants, and it was found that bilirubin is best precipitated from a dilute aqueous solution by means of a mixture of barium chloride and di-sodium phosphate, or a mixture of barium chloride and tri-sodium phosphate. For the detection of bilirubin, diazo chlorides were tried other than *p*-sulphobenzene-diazo chloride, first suggested by Ehrlich (*Z. anal. Chem.*, 1883, **23**, 275; *Centr. klin. Med.*, 1883, 721), and, later, used for the detection of obstructive jaundice, and it was found that in neutral alcoholic solution bilirubin reacted only with *p*-sulphobenzene-diazo chloride to give a highly coloured product. In an alkaline-alcoholic solution of bilirubin, both *p*-sulphobenzene-diazo chloride and *p*-nitrobenzene-diazo chloride reacted. In an acetic acid solution of bilirubin, *p*-nitrobenzene-diazo chloride yielded a highly coloured product. The colours produced were pronounced, and were stable for several days. Biliverdin showed no evidence of reacting with diazo chlorides. While the work was in progress, Greco (*Diagnostica e technica di Laboratorio*, Naples, 1931, **2**, 925) published a method which the authors have used with very good results. They were unable, however, to duplicate that part of his work in which he matched the resulting coloured solutions with solutions of mixed indicators, but describe modifications which were found to be satisfactory. P. H. P.

Relative Concentration of Esterase and Lipase in Adipose Tissue. J. S. Hepburn and H. McDuffy Moore. (*Amer. J. Pharm.*, 1934, **106**, 14–15.) The tissue was obtained from well-nourished subjects within 24 hours of death (15 days in the case of refrigerated carcases), and 50 grms. were chopped, ground with sand and triturated several times with water. The extract was filtered successively through wire-gauze and cotton-gauze, and the residue was washed until the total volume of filtrate was 500 ml. Two 100-ml. portions were then placed in separate flasks (one being boiled and cooled to serve as a control), and 1 ml. of substrate (ethyl butyrate for esterase and tributyrin for lipase) and 0·3 ml. of a 1 per cent. solution of phenolphthalein in alcohol were added. Each mixture was shaken, neutralised with 0·1 *N* sodium hydroxide solution, and preserved with 1 ml. of toluene, and the acidity was determined after 72 hours at 37·5° C. by titration with the 0·1 *N* alkali. Results for esterase and lipase, respectively, expressed as the difference between the titration values of the butyric acid produced by the sample and control were:—Chicken (3 samples), 2·10 to 2·65, 9·25 to 10·10; turkey (2), 4·40 and 4·50, 9·90 and 11·20; goose (2), 9·55 and 9·25; 8·60 and 9·00; lamb (2), 44·35 and 47·50, 19·25 and 17·80; man (2), 7·15 and 7·80, 5·50 and 5·95. J. G.

Comparative Studies of the Nutritive Value of Raw and Pasteurised Milk. J. C. Drummond. (*J. Soc. Chem. Ind.*, 1933, **52**, 400–403T.)—It is pointed out that a large proportion of papers on the nutritive value of milk in relation to pasteurisation, the conclusions of which are frequently quoted, are almost valueless when assessed in the light of the methods of scientific investigations. A series of experiments has been carried out on young rats with raw and commercially pasteurised milk. These experiments have failed to detect any evidence that pasteurisation adversely affects the nutritive value of milk. Raw milk, supplemented by biscuit prepared from white flour, has been found to be insufficient to enable a young female rat to produce and rear a normal litter of young. So far as the experiments go, they suggest that additional vitamin *B* (yeastrel) may adjust the balance of this diet so that satisfactory reproduction can occur, and it is thought that amounts of copper and iron above those required to maintain a normal blood picture may influence reproduction beneficially. It has not been determined to what extent other substances present in the yeast extract (*e.g.* manganese) may be responsible for the results observed. These results are not in agreement with those of Mattick and Golding, and no satisfactory explanation of the curious divergences from their results can be suggested; samples of the same milk and white flour employed by Mattick and Golding were used in the investigation. P. H. P.

Plant Colouring Matters. LV. Occurrence of α- and β-Carotene in various Natural Products. P. Karrer and W. Schlientz. (*Helv. Chim. Acta*, 1934, **17**, 7–8.)—According to Kuhn and Lederer (*Z. physiol. Chem.*, 1931, **200**, 246), preparations which appear to be pure β-carotene may be obtained from various plants, *e.g.* grass, ordinary nettles, spinach and paprika; also, the carotene of cows' ovaries is stated to consist of the β-form with not more than 1 per cent. of the α-modification. These results have now been tested by chromatographic adsorption with lime (Karrer and Walker, *Helv. Chim. Acta*, 1933, **16**, 641; Karrer, Walker, Schöpp and Morf, *Nature*, 1933, **132**, 26). The results show that the preparations named consist mainly of β-carotene, but are not quite free from the α-form. This accumulates in the calcium hydroxide chromatogram in a narrow, bright yellow zone below the β-carotene adsorption layer and, after solution, gives absorption spectra indicating the presence mainly of α-carotene. The small proportions of the α-form occurring in the non-fractionated, crystallised carotene preparations from spinach, paprika, nettles, and corpus luteum are insufficient to impart to them any measurable optical activity, and, for practical purposes, such preparations may be regarded as almost pure β-carotene. T. H. P.

Carotene. VII. Physical Properties of Carotenes from Different Plant Sources. J. H. C. Smith and H. W. Milner. (*J. Biol. Chem.*, 1934, **104**, 437–447.)—It has recently been shown that carotene derived from different leaves and from carrot roots possesses the same degree of unsaturation. On the basis of optical activity, however, it is clearly evident that at least two isomeric carotenes exist, namely, α-carotene, which is optically active, and β-carotene, which is optically inactive. Carotene isolated from plant sources is often a mixture of these two forms. In order to define the composition of such carotene samples in terms of their components it is necessary to know the physical properties of the mixtures, as well as of the pure components. For this reason several of the physical properties of carotene samples, varying in composition from pure α- to pure β-carotene, have been measured and compared with their optical activities. The methods of procedure for the determination of optical rotations, melting-points, solubilities and absorption spectra are described in detail. It is shown that the m.pts. of carotenes with zero optical activity average about 180·5° C. The highly rotatory α-carotene melts at 182·5° C. All the leaf carotenes examined were β-carotenes, but other workers have shown that tea leaves contain almost pure α-carotene, and that carrot leaves, in common with carrot roots, contain a mixture of α- and β-carotenes. The m.pts. of different samples of carrot root carotene were found to vary, probably depending on the relative proportions of the α- and β-forms. A series of measurements of the m.pts. and optical rotations of these samples gave a curve resembling the typical melting-point diagram for a two-component system in which solid solutions but no compounds are formed. The optically inactive carotenes from carrot root and sunflower leaf are shown to be identical. The solubility data show that solid solutions exist, that α-carotene is slightly less soluble than β-carotene, that mixtures of the two are much more soluble than either form separately, and that leaf and carrot-root carotenes have one component in common. P. H. P.

Sterols of Molluscs. W. Bergmann. (*J. Biol. Chem.*, 1934, **104**, 317–328.)—From the unsaponifiable matter of the oyster, *Ostrea virginica*, a new zoösterol, which closely resembles cholesterol, has been isolated, and has been given the name *ostreasterol.* The purest ostreasterol obtained melts at 142–143° C. and has $[\alpha]_D^{20} = -43{\cdot}57°$. It gives the Liebermann-Burchard and the Salkowski reactions, and its solubility in different solvents is about the same as that of cholesterol. Under the microscope the crystals of ostreasterol obtained from 96 per cent. alcohol appear in the form of flat needles. From methanol it crystallises occasionally in the form of well-shaped long needles. The acetate, even after one re-crystallisation, has a higher m.pt. than cholesteryl acetate. It adds bromine rapidly, giving a difficultly soluble bromide (m.pt. 122° C.). The purified bromide is reduced with zinc dust to the acetate (m.pt. 134·5° C.; $[\alpha]_D^{20} = -45{\cdot}94°$). From the purified sterol the benzoate and the propionate were prepared. The propionate melted at 113–114° C., whilst the benzoate (like cholesteryl benzoate) showed a double melting-point. At 145–147° C. it melted to a turbid liquid, which, on further heating, exhibited a play of colours, and became clear at 152° C. From the mother liquors of ostreasteryl acetate, after long standing, a crystalline acetate separated, which, after several recrystallisations and purification, melted at 104° C., and had an optical rotation of $[\alpha]_D^{21} = -15{\cdot}9°$. The sterol obtained from the acetate melted at 122° C. Until it has been more thoroughly investigated it will be referred to as ostreasterol II. Ostreasterol has been shown to replace cholesterol in all organs of the oyster. The author has also found ostreasterol in the unsaponifiable matter of the common round clam, *Venus mercenaria*, and in the mussel, *Modiola.* The investigation has been extended to members of the class of gastropods, for the common whelk and the common snail have each been shown by other workers to contain cholesterol. The sterols of the large gastropods, *Fulgur carica* and *Fulgur canaliculata*, have now been shown to contain small amounts of cholesterol and larger amounts of ostreasterol. It should be mentioned that the gastropods of the genus *Fulgur* feed largely upon oysters and other bivalves, from which food they may have acquired the ostreasterol present in their unsaponifiable matter. The analysis of ostreasterol agrees with the formula $C_{27}H_{46}O$ or $C_{27}H_{44}O$. Titration of the acetate with perbenzoic acid indicated the presence of two double bonds, which makes $C_{27}H_{44}O$ the more probable formula.
P. H. P.

Behaviour of Vitamin *C* (Ascorbic Acid) and other Reductors towards Catheptic and other Enzymes. H. v. Euler, P. Karrer and F. Zehender. (*Helv. Chim. Acta*, 1934, **17**, 157–162.)—It was noted by Karrer and Zehender (*ibid.*, 1933, **16**, 701) that ascorbic acid is able to activate catheptic enzymes from the liver previously freed from their natural activators. As a result of further experiments, various explanations seem possible for the mechanism of this action: (1) Such activation may depend on the fixation of traces of heavy metals, particularly copper, which inhibit the action of the enzymes; ferrous, ferric and calcium salts accelerate the activity of these enzymes. Activation of the inactive catheptic enzymes is also caused by substances, such as potassium cyanide, hydrogen sulphide, and cysteine, which are able to fix copper. (2) The action of ascorbic acid may consist in fixation of oxygen by the acid, the enzymes being thus protected from the action of oxygen. This effect would be similar to the activation of arginase by cysteine, ferrous salts, or the system cupric salt–ascorbic acid. (3) The ascorbic acid may give rise to the formation of a labile oxido-reduction system necessary for the enzymic processes. T. H. P.

Vitamin *E*. I. Some Chemical and Physiological Properties. H. S. Olcott and H. A. Mattill. (*J. Biol. Chem.*, 1934, **104**, 423–435.)—The only published systematic investigation of vitamin *E* is that of Evans and Burr (*Mem. Univ. California*, 1927, 8). Various aspects of the chemical and physiological problems concerned with vitamin *E* have been examined by the authors during the course of four years. The most striking function of vitamin *E* is to provide for a normal gestation in a pregnant rat, in that it prevents the resorption of the embryos which invariably occurs in its absence. A curative method of assay which was developed by Evans and Burr, based upon this physiological property, was used in the experiments described. It is shown that a single large dose of vitamin *E* given to female rats may secure fertility for two gestations, but not for three. Mothers on a diet deficient in vitamin *E* require more than 8 per cent. of yeast in the diet for normal lactation. The paralysis in the young cannot be cured by the administration of vitamin *E* after the symptoms have appeared; spontaneous recoveries have been observed. An active concentrate was prepared from lettuce by methods of fractional crystallisation and distillation, and a shortened method is described for the preparation of concentrates from wheat-germ oil by similar procedures. Some of the properties of these concentrates are tabulated. Vitamin *E* is destroyed by bromination, but not by acetylation, benzoylation, mild oxidation with silver nitrate, or hydrogenation. The concentrates strongly resist saturation with hydrogen. Potassium permanganate destroys the vitamin. Concentrates of vitamin *E* are stable for as long as four weeks in a rancid food mixture at room temperature. When injected subcutaneously, vitamin *E* has no effect on the ovaries, uterus, opening of the vagina, or cornification in the immature rat. It is also shown that there is no immediate relationship between xanthophyll and vitamin *E*. P. H. P.

Bacteriological

Significance of True *Bacillus Coli* (*B. coli communis*) and *Bacillus lactis aerogenes* in Samples of Milk. C. H. Chalmers. (*Zentr. Bakt.*, 1934, **89**, 459–474.)—These two organisms are widely distributed in nature, and have been shown to be present in samples of milk in about equal numbers. The true *B. coli* is the predominant coliform organism in fresh faeces and gains entrance to milk from this source. *B. lactis aerogenes*, on the other hand, is the predominant coliform bacillus in the dust from grains and in soil and water, these being mainly responsible for the presence of the organism in milk. During the summer of 1930 an investigation was made into the cause of the persistent contamination with *B. lactis aerogenes* of samples of "certified" milk from the two farms of a single producer. Two sources of the organism were found, namely, the outside of the udder, and, intermittently, the milk duct. Owing to the capsulated nature of the organisms, ordinary methods of washing did not appear to remove them from the udder, and washing with a mild disinfectant became necessary; a mixture of Izal (0·5 fluid oz. per gallon of water) and soft soap (3 oz. per gallon of water) proved satisfactory. Rejection of the normal amount of fore-milk did not overcome the contamination of the milk.

B. lactis aerogenes does not seem, at least when present in water, to be deleterious from the dietetic aspect, little danger accruing from the ingestion of the organism in large numbers. Moreover, Gray (*J. Hyg.*, 1932, **32**, 132) regards a preponderance of this bacillus over *B. coli* in a water-supply as an indication of freedom from pathogenic organisms, including *B. typhosus* and *B. para-typhosus B*. As the sources of contamination of water and of milk with coliform organisms are fundamentally the same, Gray's conclusion seems applicable also to milk.

From a study of the literature on *B. lactis aerogenes*, it seems desirable that the presumptive *B. coli* test should be modified to show to what separate extents true *B. coli* and *B. lactis aerogenes* are present in milk. Such modification exhibits difficulties, primarily because the different strains of coliform organisms which ferment lactose are numerous and their differences small. Help is, however, obtainable from the use of telluric acid and Brilliant Green. True *B. coli* (those which are V.P.* and Koser† negative and M.R.§ positive) resist telluric acid in certain concentrations, but are inhibited by Brilliant Green, whereas those organisms which tolerate Brilliant Green (*i.e. B. aerogenes*) do not withstand telluric acid. The concentration 0·0013 per cent. of telluric acid in bile salt solution, appears to produce the minimum inhibition of true *B. coli* coincident with prevention of the growth of *B. aerogenes*, provided that this is not present in excessive numbers. Moderately satisfactory results have been given on examination of milk samples in this way, but certain of the factors involved, concerned chiefly with the rates of growth of the two organisms, require further investigation.

T. H. P.

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* Voges-Proskaner test for acetal-methyl-carbinol. † Test for decomposition of citric acid.
§ Final reaction in glucose broth rendered acid to methyl red.

Organic Analysis

Determination of the Position of the Double Linking. R. Frognier and F. van Goetsenhoven. (*Bull. Soc. Chim. Belg.*, 1933, **42**, 391–409.)—The conditions governing the determination of the double linking in derivatives of the butenoic acids have been investigated. The readiness with which a double linking is saturated is influenced in varying degree by the nature and proximity of certain functional groupings. It is, for instance, possible to determine $\beta\gamma$-unsaturated compounds in presence of $\alpha\beta$-compounds by measuring their bromine absorption. Methods applicable to nitriles cannot, however, be used for acids, since the reactivities of these two classes of compounds are quite different. The rate at which bromine (in carbon tetrachloride solution) is added in the dark to the following compounds (also in carbon tetrachloride) diminishes in the order: vinylacetic acid, ethyl vinylacetate, vinylacetonitrile, crotonic acid, *trans*-crotononitrile, *cis*-crotononitrile. Conditions have been determined in which the numbers of molecules of bromine added per molecule of substance are for: ethyl vinylacetate, 0·99; vinylacetonitrile, 0·99; *trans*-crotononitrile, 0·016; *cis*-crotononitrile, 0·006; ethyl crotonate, 0·02.

On the basis of these results, the following modification of Heim's method (ANALYST, 1931, **56**, 129) is given for the determination of $\beta\gamma$-unsaturated esters or nitriles in presence of $\alpha\beta$-compounds. Use is made of an Erlenmeyer flask with a hollow ground-in stopper, through which passes the stem of a separating funnel. The bulb of this funnel is connected with the stopper by a second tube provided with a stop-cock. Bromination is effected by means of a solution containing 2·7835 grms. of potassium bromate and 9·918 grms. of potassium bromide per litre. The nitrile or ester (0·01 molecule) to be determined is dissolved in carbon tetrachloride (100 ml.). About 40 ml. of the bromide-bromate solution and 10 ml. of the ester or nitrile solution are run into the flask, which is at once fitted with the separating funnel and covered with a black cloth. After addition of 25 ml. of 10 per cent. sulphuric acid solution, the flask is shaken vigorously for two minutes, after which, by suitable manipulation of the two taps, 20 ml. of 10 per cent. potassium iodide solution are introduced. After further shaking for one minute, the flask is uncovered and the liberated iodine is titrated with 0·1 *N* sodium thiosulphate solution. Variations in the temperature between 0° and 30° C. do not influence the results. The amount of bromine absorbed (expressed as ml. of the thiosulphate), when multiplied by 5, gives the percentage of $\beta\gamma$-nitrile or ester in the liquid tested. Hundreds of determinations made in this way have given results reproducible to within about 0·2 per cent.

A second procedure, in which a solution of bromine (6 grms. per litre) in carbon tetrachloride is used, is also described. With this solution the vapour pressure of the bromine is much less than in aqueous solution, so that a simple Erlenmeyer flask with a ground stopper may be employed. Results reproducible to within about 0·5 per cent. are thus obtainable. T. H. P.

Detection of Nitrobenzene and of Phenol by the Formation of Resorufin. H. Eichler. (*Z. anal. Chem.*, 1934, **96**, 21–22.)—The fact that, when heated with resorcinol (or phenol) in concentrated sulphuric acid solution, nitrobenzene yields resorufin, may be utilised for the detection of either nitrobenzene or phenol. To detect nitrobenzene, a very small amount of the substance to be tested is heated with resorcinol and sulphuric acid (a solution of 0·5 to 0·6 grm. of resorcinol in 100 grms. of the concentrated acid is suitable) until the liquid becomes violet or emits sulphur trioxide vapour. After being cooled, the solution is diluted with water, made alkaline with sodium carbonate, and filtered if necessary; the appearance of the yellowish-red fluorescence accompanying the formation of resorufin indicates the presence of nitrobenzene in the substance. Phenol is tested for by heating with nitrobenzene in concentrated sulphuric acid solution. A number of nitro-compounds are specified which do not give resorufin when treated with resorcinol as described above. T. H. P.

Determination of Pyruvic Acid. G. Carpeniseanu. (*Compt. rend.*, 1934, **198**, 272–274.)—Simon's colorimetric determination of pyruvic acid, based on the green colour given with acetic acid, sodium nitroprusside, and ammonia (*Comp. rend.*, 1897, **125**, 534; *Bull. Soc. Chim. Biol.*, 1924, **6**, 477), is capable of greatly increased sensitiveness if the conditions are suitably adjusted. The author uses a wide range of standards prepared from a solution (*P*) containing either 0·25 grm. of sodium pyruvate or 0·2 grm. of pyruvic acid per litre. The quantities measured out are run from burettes calibrated to 0·5 ml., and the colour comparisons are made in test-tubes (about 25 ml.) free from striae and of the same dimensions. The standard tubes contain: 1 ml. of water; 0·95 ml. of water and 0·05 ml. of solution *P*; 0·09 ml. of water and 0·1 ml. of solution *P*; . . . 1 ml. of solution *P*. A tube with 0·1 ml. of the solution to be tested is also prepared. To each tube are added, in order, 0·25 ml. of acetic acid (40 vols. of glacial acetic acid + 60 vols. of water), 0·5 ml. of fresh sodium nitroprusside solution (1 per cent.) and 0·75 ml. of ammonia solution (1 vol. of 0·880 ammonia + 1 vol. of water). After the lapse of 30 to 60 minutes for the more concentrated tubes, or 60 to 90 minutes for the others, the tubes are compared by looking through them at a piece of white paper.
T. H. P.

Tung Oil. Chemical Studies and Specification. L. A. Jordan. (*J. Soc. Chem. Ind.*, 1934, **53**, 1–11T.)—The chemical work carried out by the Paint and Varnish Research Association in connection with the plans for Empire development, as co-ordinated by the Tung Oil Committee of the Imperial Institute, has involved, in addition to the examination of chemical and physical properties of tung oils as related to the country of origin, species, manurial and cultivation factors, methods of crushing, etc., concurrent work, which has been carried on for 3 years with a view to a better understanding of such matters as the state of polymerisation, and the present paper gives an account of this work. Tung oil has been shown to consist mainly of the glycerides of the triply unsaturated elaeostearic acid, the singly unsaturated oleic acid, and the saturated stearic acid, the elaeostearic glyceride being mainly responsible for the characteristic properties of the oil. This glyceride has now been determined, together with the relative proportions of the other glycerides, the total unsaturation being measured by means of complete hydrogenation, and partial saturation by the addition of halogen to the oil in various ways.

Complete saturation determination involved the examination of the method used for finding the iodine value. Although the quantity of hydrogen used to effect saturation of a quantity of tung oil can be determined within 1 per cent., the experimental refinements preclude the method being adopted in commercial specifications. For the measurement of partial saturation a modification of Kaufmann's mixed halogen method has been followed. Gelation effects are discussed in detail. For the evaluation of the degree of polymerisation of a tung oil it is emphasised that the past of a treated tung oil determines its present and future possibilities, so that the manner of expressing the degree of polymerisation can only be a statistical average. However, a definite proportion of the gel is insoluble in acetone, the proportion increasing with the time of heating, up to an uncertain limit, approximately 75 per cent. of the mass. The measurement of the amount and state of the polymerisable content of tung oil at any time can be followed by studying the changes in the amount of acetone-insoluble material, or disperse phase in the polymerised oil, and the refractive index and viscosity of the oil and its component phases. The "heat tests," which in some form comprise a feature of every specification for tung oil, involve either heating small quantities of oil in a hot bath or the direct heating of large quantities of oil. Small quantities are preferable, so that the start of the polymerisation change may be a well-defined instant. The "polymerisable matter" was found to vary with the condition of the test, and it was considered desirable to select a precise period for after-heating of the gel, at the end of which the rate of change with time is small, and within an ordinary degree of experimental error. A period of 20 minutes was selected, at which, with a polymerising temperature of 290° C., the percentage extract is at a minimum. The following is the final "Heat Test and Determination of Polymerisable Matter in Tung Oil" recommended for inclusion in the British Standard Specification; it has been in use for some time at the Paint Research Station:—The oil (5 ml.) is placed in a thin test-tube (not over 0·04 in. in thickness, 6 in. by ⅝ in. internal diameter), fitted with a grooved cork through which a glass rod, ⅛ in. in diameter, may freely pass. The tube is placed in an oil-bath previously heated to 295° C., which causes the temperature to drop to 290° C., at which point it is kept (±1°) by regulating the source of heat. The oil-bath consists of an 800-ml. glass beaker (4 in. diameter, 5 in. high), filled to a height of 3 in. with soya bean, cotton-seed or mineral oil (approx. 500 ml.), and heated by means of a gas burner (on a gauze); the oil is not stirred. The beaker is provided with a loose metal cover with two ¾-in. holes symmetrically placed ¾ in. from the centre. The tube, with the tung oil, is supported through one hole by a cork collar arranged to keep the bottom of the tube 1 in. above the bottom of the bath, and the second hole carries a cork holding the thermometer (of a limited range pattern) immersed to within 1 in. above the reading 290° C. (a detailed specification for a suitable thermometer is given), and with its bulb 1 in. above the bottom of the bath. Seven minutes after the insertion of the sample the glass rod is raised to test for gelation, and this test is repeated every ¼ minute until the tube is lifted with the rod. This stage should be reached within 10 minutes with a genuine tung oil. The sample is then left undisturbed in the bath, with the temperature at 290° C., for 20 minutes from the outset of gelation, and is then withdrawn, left to cool in a vertical position in air with the cork removed, after the outside of the tube has been wiped free from oil. The oxidised top surface (¼ in. in depth) is cut off, the remainder roughly crumbled, and a 2-grm. portion is weighed into a mortar, ground with a little sharp sand, extracted in a Soxhlet extractor for 1 hour with petroleum spirit (60°–80° C.), after which the solvent is evaporated, and the residue weighed. Results obtained by independent workers agreed well. An example of results is as follows:—Gelation time (*a*), extractive per cent. (*b*) and $n_D^{25°C}$ (*c*). Pure American *A. Fordii* oil, (*a*) 8¼ mins., (*b*) 16·3, (*c*) 1·5187; ditto +5 per cent. soya bean oil, (*a*) 8½, (*b*) 20·3, (*c*) 1·5167; commercial tung oil, (*a*) 9½, (*b*) 21·8, (*c*) 1·5172; oil of *A. montana*, (*a*) 11, (*b*) 27·9, (*c*) 1·5145; ditto +10 per cent. of soya-bean oil, (*a*) 12½, (*b*) 36·9, (*c*) 1·5112. It has been found that the extent of change in results due to experimental variations can be approximately foreseen. The temperature of 290° C. is taken because the effect of temperature variations on the extractive determination is least at this point. The possibility of establishing an empirical connection between extractive-content and commercial valuation of the oil is suggested. The newer grades of orchard-grown tung oil, characterised by quick gelation and high insoluble-content, appear to yield slightly superior varnish media when the tung oil is first adulterated with about 5 per cent. of a semi-drying oil, such as soya-bean oil. D. G. H.

Analysis of Nitrocellulose Lacquers. H. Anderson. (*J. Soc. Leather Trades Chem.*, 1934, **18**, 88.)—The lacquer (10 to 15 grms.) is treated with a large excess of benzene, added slowly and with vigorous stirring. The precipitated nitrocellulose is collected on a tared filter paper, washed with benzene, dried and weighed. This mixture of nitrocellulose and pigment is digested with 200 ml. of acetone, and the pigment collected on a tared filter paper, washed, dried and weighed. A pigment consisting of a lake colour leaves a white ash, if any. The benzene solution (*supra*) is dried in a steam-oven. Boiling it with dilute borax solution will remove any shellac; and extraction with cold alcohol removes plasticisers, such as synthetic or formaldehyde-phenol resin, but not gum dammar. Phosphorus in the plasticiser may indicate tricresyl phosphate; phthalic acid would suggest dibutyl phthalate; acetic acid, triacetin; and benzoic acid, glyceryl tribenzoate. Oxalic acid would point to "Barkite," and adipic acid to "Sipalin." Alternatively, plasticisers and gum may be differentiated by adding 20 ml. of water to 20 grms. of the lacquer, evaporating the mixture to dryness, and heating the residue for at least 3 hours in a steam-oven to remove solvents of high b.pt., and then digested with cold alcohol or dilute borax solution, as described above. The type of solvent may be ascertained by steam-distillation, and drying and fractionating the distillate. R. F. I.

Inorganic Analysis

Detection of Cations by means of Resorufin. H. Eichler. (*Z. anal. Chem.*, 1934, **96**, 22.)—With solutions of the salts of certain elements, alkaline solutions of resorufin give characteristic, coloured precipitates which appear dark in the deep yellowish-red fluorescent solution in incident light (especially when a black background is used), and are hence detectable in small quantity. The neutral or faintly acid solution of the salt is treated with a few drops of a solution of 0·2 grm. of resorufin in 5 ml. of ammonia solution and 100 ml. of water. Solutions containing $Cu^{\cdot\cdot}$, $Cd^{\cdot\cdot}$, $Fe^{\cdot\cdot\cdot}$, $Al^{\cdot\cdot\cdot}$, $Cr^{\cdot\cdot\cdot}$, $Ni^{\cdot\cdot}$, $Zn^{\cdot\cdot}$, $Ba^{\cdot\cdot}$ or $Sr^{\cdot\cdot}$ give precipitates, and solutions containing $Mg^{\cdot\cdot}$, $Ag^{\cdot}$, or $Pb^{\cdot\cdot}$ and free from ammonium salts yield violet precipitates. Ferrous salts (or hydrosulphites) reduce the resorufin and must be oxidised (or destroyed by treatment with acid) prior to the test. Freshly precipitated ferric or aluminium hydroxide also reacts with resorufin. T. H. P.

Determination of Uranium in Ores. W. R. Bennett. (*J. Amer. Chem. Soc.*, 1934, **56**, 277–280.)—*Swedish Kolm.*—The method involves removal of iron by electrolysis over a mercury cathode, precipitation of titanium with cupferron, and volumetric determination of uranium with permanganate. To a 3·5-grm. sample of the ignited ore, contained in a platinum dish, are added 10 ml. of concentrated sulphuric acid and (drop by drop) 15 ml. of hydrofluoric acid, the mixture is digested on a steam-bath for half an hour, and then heated for two hours at a temperature sufficient to cause the evolution of sulphur trioxide fumes. After cooling, 100 ml. of water are added, the mixture is heated to dissolve soluble material, then filtered, and any residue is given a second treatment with sulphuric and hydrofluoric acids. If a little residue still remains, it is brought into solution by fusion with potassium bisulphate. The combined solution is diluted to 500 ml., and the elements of the ammonium hydroxide group are precipitated by the addition of ammonia in the usual way. The precipitate, which contains the uranium, is filtered off and dissolved in 18 ml. of 6 *N* sulphuric acid, and the solution is diluted to 50 ml., giving an acid concentration of 2 to 3 per cent. by volume. The solution is electrolysed over a mercury cathode with a current of 2 to 3 amps. at 8 volts for 2½ hours (*cf.* Smith, "Electroanalysis"). After electrolysis, sulphuric acid is added to the solution to give an acid concentration of about 10 per cent. by volume, and the uranium is oxidised to the sexavalent condition by the addition of a slight excess of potassium permanganate. Titanium is then precipitated by cupferron in the usual way, and the precipitate, after being washed, is rejected. The filtrate is evaporated with nitric acid to destroy the cupferron, the evaporation being continued until only 5 ml. of sulphuric acid remain. This residue is dissolved in 100 ml. of water, and sufficient potassium permanganate is added to the warm liquid to yield a permanent pink colour. The solution is cooled, passed through a Jones reductor; air is bubbled through this reduced solution for 5 minutes to oxidise any tervalent uranium to the quadrivalent form, and the solution is finally titrated with standard permanganate. The addition of a few drops of 0·5 *M* barium diphenylamine sulphonate indicator is recommended to render the end-point readily detectable in the green-coloured uranium solution.

Canadian Uraninite.—This mineral contains rare earths, *e.g.* cerium, and metals of the hydrogen sulphide group; a modified method was, therefore, adopted. A 0·5-grm. sample is heated with 10 ml. of concentrated nitric acid and 10 ml. of concentrated sulphuric acid; the mixture is evaporated to 3 ml.; this is taken up in 100 ml. of water and saturated with hydrogen sulphide at 60° C. The resulting sulphide precipitate is filtered off, washed and rejected, and the filtrate is boiled to expel hydrogen sulphide. The rare earths are precipitated from the solution by the addition of hot saturated oxalic acid solution, the oxalate precipitate being kept overnight and then filtered off. The solution is electrolysed as above, and the solution is evaporated with nitric acid to destroy any oxalic acid which remained undecomposed after the electrolysis. The residue is dissolved in water. The method from this point is the same as for Swedish Kolm. S. G. C.

Direct Determination of Iron in Presence of Vanadium by the use of a Silver Reductor. G. H. Walden, L. P. Hammett and S. M. Edmonds. (*J. Amer. Chem. Soc.*, 1934, **56**, 350–353.)—Iron and vanadium in dilute hydrochloric acid solution are reduced by finely divided silver to the bi- and quadrivalent states, respectively; in this reduced solution, rendered 5 *M* acid with sulphuric acid, the ferrous iron may be quantitatively oxidised with ceric sulphate, whilst the vanadium remains unoxidised. The silver reductor is of the Jones reductor type, employing a column (12 cm. by 2 cm.) of silver, precipitated from a solution of 29 grms. of silver nitrate in 400 ml. of water by means of sheet copper; the silver column is supported in a glass tube over a plug of glass-wool and no suction is required. In the course of use the silver is converted into silver chloride, which blackens; the blackening gradually extends down the column in successive determinations, thus affording an indication of the behaviour of the reductor; when the blackening extends over three-quarters of the length of the column, the silver should be regenerated by inserting a zinc rod into the reductor tube, so that it touches the contents, thus reducing the silver chloride back to silver without loss. *Method.*—The test-solution (50 ml.; *M* in hydrochloric acid) is poured through the reductor at the rate of 30 ml. per minute; the column is then washed through with 150 ml. of *M* hydrochloric acid. To the combined liquids are added 200 ml. of 10 *M* sulphuric acid; after cooling, 1 drop of 0·025 *M* "phenanthroline-ferrous ion" indicator is added, and the solution is titrated with 0·1 *M* ceric sulphate solution. Accurate results were obtained in test experiments with about 0·1 grm. of iron in presence of approximately equal amounts of vanadium, manganese, titanium and chromium, and also with about 13 mgrms. of iron alone and in presence of a similar amount of vanadium; molybdenum interferes. Good results were obtained with solutions of ferrovanadium after removal of the molybdenum, which involved separation of the iron and vanadium by double precipitation with ammonia. As much as 0·2 grm. of nitric acid may be present in 50 ml. of the solution to be reduced, since, unlike the zinc reductor, the silver reductor yields no reduction products of nitric acid capable of being oxidised by ceric sulphate. S. G. C.

Detection of Nitrates, Nitrites, and Nitrosylsulphuric Acid by the Formation of Resorufin, Orcirufin, and Indophenols. H. Eichler. (*Z. anal. Chem.*, 1934, **96**, 17–21.)—Small proportions of nitrites and nitrates may be detected, even in presence of coloured substances, by means of the reaction between resorcinol (or orcinol) and nitrosylsulphuric acid, which gives, first, nitroresorcinol and the corresponding indophenol, and then, by ring-closure (in presence of hot, concentrated sulphuric acid), resorufin. This is characterised by the violet colour of its solution in concentrated sulphuric acid and by the yellowish-red fluorescence of its violet-red alkaline solution. Use is made of a solution of 0·5 to 0·6 grm. of resorcinol in 100 grms. of concentrated sulphuric acid free from the nitrosyl-acid (*cf.* Atkins, *Nature*, 1932, **129**, 98); a blank test must be made on each fresh batch of this solution. From 1 to 2 ml. of this solution is poured as a layer on to a little of the substance to be tested; any reaction—such as evolution of carbon dioxide, sulphur dioxide, etc.—is allowed to finish, and the liquid is then heated until either a violet colour indicative of nitrite or nitrate appears or sulphur trioxide vapour is evolved. After being cooled, the solution is diluted with 5 to 10 ml. of water and neutralised with sodium carbonate. Any precipitated carbonate or hydroxide is either filtered off or allowed to settle, the yellowish-red fluorescence of the resorufin being then readily visible either in sunlight or in front of a dark background. The solution must not be made alkaline with sodium hydroxide, which decomposes resorufin. The resorcinol solution used may be replaced by a solution of 0·4 to 0·5 grm. of orcinol in 100 grms. of concentrated sulphuric acid, which gives a red colour with nitrite or nitrate when heated on the water-bath.

The formation of resorufin is prevented if iron, sulphides, or comparatively large proportions of oxidising agents, such as chromates, manganese dioxide, iodates, or nitrates, are present. Such interference may be avoided by heating the substance for a long time with concentrated sulphuric acid, cooling the liquid, adding sufficient solid resorcinol to produce a blue colour, and then heating until the solution becomes violet.

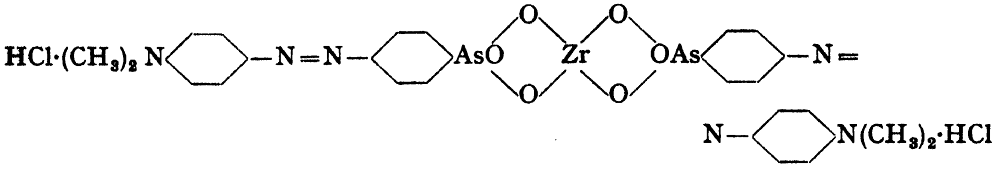
When both nitrite and nitrate are present, the nitrite may be removed, prior to the test, by evaporating a faintly acid or faintly alkaline solution of the substance. A suitable procedure is to bring the solution to p_H 3 by addition of acetic acid, or to add ammonium chloride or sulphate before evaporation. Another method consists in destroying the nitrite by treatment with urea in slightly acid solution. In any of these ways nitrate may be detected in presence of nitrite, but nitrite can be detected only in absence of nitrate. The method is easily adapted to the detection of nitrosylsulphuric acid or oxides of nitrogen. As little as 0·000015 grm. of sodium nitrite is detectable by this reaction with resorcinol. T. H. P.

Use of Magdala Red for the Detection of Nitrites. H. Eichler. (*Z. anal. Chem.*, 1934, **96**, 99–100.)—The reagent is a 0·1 per cent. solution of the dye in water containing a little acetic acid. A minimum quantity of the reagent is added to 5 or 10 ml. of water, which is treated in the cold with hydrochloric acid until fluorescence ceases and the liquid turns violet. The solution is heated to boiling, which causes strong yellow-red fluorescence, and the neutral or feebly alkaline solution is added. If nitrite is present, the fluorescence again disappears, while the colour changes to blue. Cupric and ferrous salts favour the reaction; nitrates do not interfere with the fluorescence, even on long boiling, but sulphites and thiosulphates destroy it. Formaldehyde is without effect. W. R. S.

Microchemical

Collected References. Micro-methods of Determination of Proteins in Medicine and Biology. A. Wasitzky. (*Mikrochem.*, 1934, **14**, 81–112.)—Details of the more important methods are given under the following headings:—(i) Gravimetric methods. (ii) Kjeldahl methods. (iii) Refractometric, interferometric, and combined refractometric and viscometric methods. (iv) Diaphanometric and nephelometric methods. (v) Colorimetric methods. (vi) Sedimentation methods. (vii) Volumetric methods. (viii) Other methods. There are 102 references to original papers. J. W. B.

"Spot" Test for Fluorine. F. Feigl and E. Rajmann. (*Mikrochem.*, 1933, 12, 133–136.)—The *p*-dimethyl-amino-azo-phenyl-arsenic acid test for zirconium, in which the following yellow-brown acid insoluble compound is formed:



is used as a test for fluorides, which decolorise this compound and liberate the free azo-phenyl arsenic acid, which is red. The reagent consists of a 0·025 per cent. solution of *p*-dimethyl-amino-azo-phenyl-arsenic acid in 9 parts of alcohol and 1 part of concentrated hydrochloric acid. Quantitative filter paper (Schleicher and Schull, 589) is immersed in this solution for a few minutes, dried in air, and then immersed in a solution of zirconium oxychloride (containing 0·01 per cent. of zirconium) in N hydrochloric acid, which turns the red paper brown. After ten minutes the paper is washed for five minutes with cold 2 N hydrochloric acid, then for five minutes with 2 N hydrochloric acid at 50° C., and finally with water, alcohol and ether, and dried *in vacuo*. For the test, three drops of neutral or alkaline test solution are acidified on a spot plate or in a micro-crucible with a drop of 2 N hydrochloric acid, and one drop of this mixture is placed on the impregnated paper. In the presence of fluorides a colourless centre appears surrounded by a red circular fleck. As little as 0·25 γ of fluorine can be detected in a dilution of 1:200,000. In the presence of phosphates, arsenates, sulphates and thiosulphates, which interfere, and also with minerals and insoluble fluorides, the fluorine is first converted into hydrogen silicofluoride. Feigl's closed test-tube (Feigl, *Qualitative Analyse mit Hilfe von Tüpfelreaktionen*, Leipzig, 1933, p. 121) is used; the solid substance under examination is placed at the bottom of the tube and covered with a few drops of concentrated sulphuric acid; a few drops of dilute hydrochloric acid are placed on the dropper on the underside of the stopper, and the apparatus is gently heated on an asbestos plate. To prevent distillation of the sulphuric acid, owing to too prolonged heating, a crystal of tartaric acid may be placed in the sulphuric acid. After one or two minutes' heating the drop of hydrochloric acid under the stopper is tested for fluorides by placing it on the reagent paper, as before. In this way as little as 0·2 γ of fluorine in the presence of 80,000 times the amount of foreign matter can be detected. J. W. B.

Micro-Volumetric Analysis with Diphenylcarbazide and Diphenylcarbazone as Indicators in Mercury Titrations. J. V. Dubský and J. Irtílek. (*Mikrochem.*, 1933, 12, 315–320.)—Both diphenylcarbazide and diphenylcarbazone are used as indicators in 2 per cent. alcoholic solution, rendered colourless, if necessary, by a few drops of 0·2 N nitric acid. Metallic salts other than those of mercury (with the exception of chromates and molybdates) do not react with the reagents in 0·2 *N* nitric acid, so that the indicators may be used in the presence of other heavy metals. Diphenylcarbazone is the more sensitive reagent; it gives an intensive violet-blue colour with the first micro-drop of excess of mercuric nitrate in a chloride titration. For a chloride determination, a few mgrms. of the substance to be analysed are dissolved in a few ml. of water, and 1 ml. of 0·2 *N* nitric acid and 3 drops of diphenylcarbazide (or carbazone) are added. For the titration, 0·01 *N* mercuric nitrate is run in from a micro-burette. Results of test determinations agreed with the calculated values within less than 0·3 per cent. J. W. B.

α-α'-Dipyridyl as a Reagent for the Determination of Ferrous and Total Iron in Natural Waters. H. Müller. (*Mikrochem.*, 1933, **12**, 307–314.)—*Reagents*: A 1 per cent. solution of α-α'-dipyridyl in 0·1 *N* hydrochloric acid; hydrochloric acid 0·1 *N*, solid (A.R.) crystallised sodium sulphite; a 10 per cent. solution of sodium sulphite; dilute hydrochloric acid (1: 1). *Iron standard solution*: A solution of 0·4318 grm. of ferric ammonium sulphate with 10 ml. of concentrated hydrochloric acid, diluted to 1 litre. This is used in two dilutions: (i) consists of 160 ml. of the standard solution, and 2 ml. of 5 per cent. mercuric chloride solution diluted to 1 litre, and (ii) consists of (i) diluted 10 times. These solutions contain 8·0 γ and 0·8 γ per ml., of iron respectively. The colour formed is permanent; hence a series of permanent standard colours are made up and kept in stoppered tubes of colourless glass, 14 cm. high and 1 cm. in diameter, graduated by means of a ring at a height of 10 cm. The standard colours are made up from volumes of 0·2 to 6 ml. of dilution (ii) and 0·65 to 1 ml. of dilution (i), mixed with 2 ml. of α-α'-dipyridyl solution, followed by a few ml. of the sodium sulphite solution and 0·1 ml. of dilute (1: 1) hydrochloric acid, and are made up to the mark with sodium sulphite solution. After shaking, two drops of the mercuric chloride solution are added, and the mixture is shaken again. The ferrous iron in the solution under examination, after the same treatment, is compared directly with the standard colours. The total iron may be determined afterwards in the same solution, after adding about 0·6 grm. of solid sodium sulphite and about 0·1 ml. of hydrochloric acid. The standard solutions are similarly treated, and the colours are matched after about 5 minutes. The smallest determinable amount of iron in 8 ml. is 0·1γ. Results for the water of a number of lakes are given. J. W. B.

Physical Methods, Apparatus, etc.

Mercury-in-Glass Thermo-regulator. C. C. Coffin. (*Proc. Nova Scot. Inst. Sci.*, 1933, **18**, 213–214.)—A closely-wound helix (16 turns) of flattened, thin-walled glass tubing, filled with distilled mercury, is placed in the bath in such a way that the ends project vertically above the surface of the liquid. One end contains a stop-cock (below the liquid surface) and, below it, a pointed platinum or tungsten contact, whilst the other is sealed to a capillary tube (0·3 mm. in diameter), in which is fixed a second contact also below the surface; on the latter contact is fused a glass bead which serves to maintain a central position. The stop-cock regulates the amount of mercury in the system and, consequently, the setting; the capillary may be open to the air, except in cases where a high current causes sparking to occur, when it may be used to fill the system with an inert gas. The mercury in such an apparatus should form a column about 160 cm. long, 0·8 cm. wide and 0·15 cm. thick, and it would then have a volume 20 times, and a surface-volume ratio 3 times those of an ordinary Beckmann thermometer. Advantages are: ease in filling, a wide temperature-range (since mercury is used), efficient integration of temperature over the whole volume of liquid in the bath, elimination of inflammable liquids, simple adjustment, and the fact that little room is occupied in the bath. The dv/dT ratio is much less than for toluene, but this is offset by the greater rate of change of volume; and in a steel spiral this would probably be even greater. The accuracy of regulation is 0·001° C.

J. G.

Examination of Rye-Grass Seed by Means of Ultra-Violet Light. L. François. (*Ann. Falsific.*, 1934, **26**, 34.)—In order to distinguish the seeds of English rye grass (*Lolium perenne L.*) from the Italian species (*Lolium italicum* Al. Br., *Lolium multiflorum Lam.*), especially in cases in which the distinguishing prolonged awn of the inferior glumule in the Italian species has been broken off, the samples of seeds are germinated, and the young radicles are examined under ultra-violet light. The Italian seed shows a brilliant silver-blue fluorescence, but the English remains dull, with no trace of fluorescence. D. G. H.

Rapid Photometric Method for the Determination of Small Quantities of Lead. B. L. Samuel and H. H. Shockey. (*J. Assoc. Off. Agric. Chem.*, 1934, **17**, 141–146.)—The method, which involves the photometric determination of lead sulphide in suspension by means of a photo-electric cell, has been adapted to the determination of lead in foodstuffs, with special reference to sprayed apples.

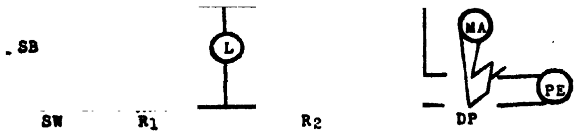


Fig. 1

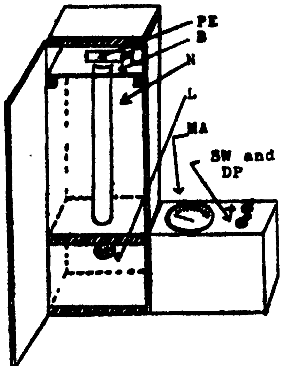


Fig. 2

The photometer (Fig. 2), which the authors constructed themselves at small cost, consists of a wooden box, the front of which opens on hinges, with the parts mounted as shown. The Nessler tube, N, stands over a hole in the lower shelf, and the top of it fits into a hole in the upper removable shelf, B. The light-bulb, L, is mounted about ½ inch directly under the Nessler tube, and the photo-electric cell, PE, is fixed above the Nessler tube. In the compartment on the right are contained the other components of the apparatus, of which the electrical connections are shown in Fig. 1: SB is a 6-volt accumulator; SW, switch; R1, 1-ohm 5-amp. variable rheostat; R2, 100,000-ohm resistance; L, 6-volt 32-candle-power electric bulb; DP, double pole-double throw switch; MA, 0 to 100 micro-ammeter; PE, Weston photronic cell, Model 594. *Method*:—The organic matter of a sample of convenient size is destroyed by digestion with nitric and sulphuric acids. The nitric acid having been removed by evaporation, the residue is cooled, dissolved in 25 ml. of water, 25 ml. of hydrazine sulphate reagent [20 grms. of hydrazine sulphate and 20 grms. of sodium bromide, dissolved in 1 litre of hydrochloric acid (1+4)] and 20 grms. of sodium chloride are added, and any arsenic is removed by distillation. The remaining liquid is transferred to a 200-ml. volumetric flask, the original vessel being washed out with 10 ml. of hot ammonium acetate solution (20 per cent.) followed by water; 10 ml. of nitric acid are added, and the liquid is made up to volume. Forty ml. of the filtered liquid are transferred to a separating funnel, and shaken with 2 ml. of ammonium thiocyanate solution (saturated) and 15 ml. of ether, to extract the iron. The aqueous bottom layer, which should be practically colourless, is drawn off, 25 ml. of ammoniacal ammonium citrate and potassium cyanide solution (a mixture of 12·5 grms. of citric acid, neutralised with ammonia, in 50 ml. with 125 ml. of 10 per cent. potassium cyanide solution and 1 litre of "ammonium hydroxide") are added, the mixture is transferred to the Nessler tube and diluted to the mark, and the tube is placed in position in the photometer. The light in the photometer having been turned on for at least 1 minute, the rheostat is so adjusted that the micro-ammeter reading is 100. Four drops of sodium sulphide solution (10 per cent.) are added, the solution is mixed by making three gentle strokes with a glass plunger, and the micro-ammeter reading is at once noted. The reading obtained is referred to a curve connecting the photometer cell current with the amount of lead present, which has been established experimentally by working under similar conditions with known amounts of lead. The instrument is sensitive to 0·013 mgrm. of lead; the agreement with the theoretical results in test experiments was within 0·06 mgrm. Phosphates and calcium do not interfere. The only common metals which interfere are bismuth, mercury and tin. The interference of tin can be overcome by the addition of 1 ml. of concentrated potassium hydroxide solution before the addition of the sodium sulphide.

S. G. C.

Reviews

SOLVENTS. By T. H. DURRANS, D.Sc., F.I.C. Monographs on Applied Chemistry. Third and revised edition. Pp. xiii + 205. London: Chapman & Hall, Ltd. 1933. 10s. 6d.

Little beyond what has already been said in this journal about the first and second editions of this book needs to be added. The addition of a further 26 pages to the book, again without any increase in price, reflects the increasing scope of the subject, with the resulting potentially wider public for the book, as well as the deserved increase in circulation of the series of monographs, of which this is volume four, produced under the editorship of Dr. E. Howard Tripp.

The reviewer's comments on the second edition have, in so far as they were critical, been largely met, but the emphasis still lies heavily on the employment of solvents in the manufacture and use of cellulose lacquers. The reviewer is still of opinion that a sub-title indicating the restricted, albeit increasingly important, scope of the book, would prevent possible misunderstanding and disappointment.

A table of plasticiser proportions has been added as a third appendix, and the chapter on "vapour-pressure" includes new sub-sections on "blush numbers" and on evaporation rates. Apart from these specific additions, an increase in the number of solvents discussed, consequent on the introduction of new ones into the industry, is mainly responsible for the additional pages. A. L. BACHARACH

NATURAL VARNISH RESINS. By T. HEDLEY BARRY. Pp. xii and 294. London: Ernest Benn, Ltd. Price 42s. net.

This work, as its title implies, is restricted to the study of only those resins which are used in the varnish and allied trades.

It is divided into two parts, the first, covering 43 pages, being devoted to the history, botanical origin, physical characters, and general methods of analysis. This part of the work is of considerable interest, and includes a good deal of information not hitherto to be found, except in a scattered form in periodicals, etc. The second part, which forms the bulk of the work, deals with individual resins, including the copals, kauri, dammar, acaroid, sandarac, mastic, dragon's blood, kino, natural lacquers, rosin and shellac. The systematic account of these resins is well done, and forms very interesting reading. The pure chemistry of such bodies as rosin and shellac is brought well up to date, and the only section one would like to see expanded is that dealing with analysis. In any future edition this could easily be extended without interfering in the slightest degree with the groundwork of the book. Dealing with the Wijs method for the determination of the iodine value of resins, the author states that it "owing to its rapidity, is frequently adopted, and in the case of shellac has become firmly established as the standard method." Since the reviewer, in 1901, showed that the then existing published figures for shellac were hopelessly incorrect, as they were obtained from, in many cases, grossly adulterated samples, the standard method for the determination of rosin in shellac in this country has not been the Wijs, but the Hübl process. The latter is far less influenced by slight changes of conditions, and is only an additive reaction, giving about half the value given by the Wijs solution. It is true that the Wijs process is official in the United States.

Four papers on shellac, which are merely referred to in two lines on page 263, contain a great deal of analytical information which is absent from the present work. No reference is made to the influence of orpiment on the iodine value of shellac, which was first established in one of the papers referred to, and which caused so many pure samples of fine orange shellac to be condemned in the United States as containing rosin. To-day this influence is well recognised in India and in America, as well as in this country. The author appears to have lost sight of the terms on which shellac is marketed in London—a matter to which he devotes some space. One illustration will suffice. TN shellac contracts for delivery, which constitute the bulk of the trade, provide for 3 per cent. only of adulterating matter: parcel to be accepted with fair allowance up to 10 per cent.: over 10 per cent. entitles to rejection.

The book will be found of considerable value to all interested in the varnish resins, but it is to be hoped that more information of value to the analyst will be forthcoming in any future edition. ERNEST J. PARRY

A TEXTBOOK OF INORGANIC CHEMISTRY. By Dr. FRITZ EPHRAIM. Second English Edition, Revised and Enlarged, by P. C. L. THORNE, M.A., M.Sc., Ph.D. Pp. xii+873. London: Gurney & Jackson. 1934. Price 28s. net.

The first English edition of this excellent treatise was reviewed in the ANALYST (1926, **51**, 651). The plan there outlined has remained unaltered; the text-matter is subdivided into seven sections, each of which has been brought up to date so as to include the most recent discoveries and theories. These additions to chemical knowledge are responsible for an increase of 68 pages.

The most interesting new-comers in the new edition are: The elements rhenium and masurium, both higher homologues of manganese; illinium (or florentium), the elusive member of the cerium group; alabamine, homologue of iodine; and virginium, homologue of caesium. It must be added that the individuality of the last two requires confirmation. We are also introduced to the binary compounds, fluorine monoxide (obtained by the action of fluorine upon caustic soda) and sulphur tetroxide (formed in the fluorination of sulphuric acid).

Throughout the book the reader is made aware of the steady progress of chemical science during the brief interval which has elapsed between the appearance of the two English editions. To name only a few advances, we are presented with the most recent views on the structure of atoms, ions, molecules, and crystals; on ionic volume and the parachor; on the constitution of the boron hydrides; on the properties of the rare earths and the lanthanide contraction. A considerable advance in our knowledge of the structure of silicates has been realised as the result of Bragg's X-ray analysis and the investigations of Goldschmidt on isomorphism. The conclusions arrived at by these two chemists are summarised in Chapter XXVII.

In these times of rapidly increasing knowledge and unavoidable specialisation, a textbook, such as the one under review, has become indispensable. It enables students and professional chemists to survey and retain their grasp of general chemistry, while reference books, such as Dr. Mellor's monumental work and the German handbooks (*e.g.* Gmelin-Kraut), record all that is known about the individual compounds. Of textbooks of the former type, a new edition is necessarily required at intervals of less than ten years. English-speaking chemists are fortunate to possess in this attractive volume Dr. Thorne's masterly translation of the fourth German edition. It is to be hoped that Ephraim's work will continue to appear in both languages whenever the need for a revised edition arises.

W. R. SCHOELLER

Publications Received

PHYSICO-CHEMICAL METHODS. By J. REILLY and W. N. RAE. With a Foreword by F. G. DONNAN. London: Methuen & Co., Ltd. 1934. Price 42s. net.

TECHNICAL GAS ANALYSIS. By G. LUNGE. Revised and re-written by H. R. AMBLER. London: Gurney & Jackson. 1934. Price 21s. net.

A TEXT-BOOK OF INORGANIC CHEMISTRY. (Edited by J. NEWTON FRIEND.) Vol. VI, Part II. PHOSPHORUS. By E. B. R. PRIDEAUX. London: Chas. Griffin & Co., Ltd. 1934. Price 18s. net.

A MANUAL OF PRACTICAL INORGANIC CHEMISTRY. By E. H. RIESENFELD. Translated by P. RÂY. Calcutta: Chuckervertty, Chatterjee & Co. 1933. Price 9s.

THE DESIGN AND CONSTRUCTION OF HIGH PRESSURE CHEMICAL PLANT. By H. TONGUE. London: Chapman & Hall. 1934. Price 30s. net.

ANNUAL REPORTS OF THE SOCIETY OF CHEMICAL INDUSTRY ON THE PROGRESS OF APPLIED CHEMISTRY. 1933. Vol. 18. Price 7s. 6d. to members, 12s. 6d. to others.

THE ATOM. By J. TUTIN. London: Longmans, Green & Co., Ltd. 1934. Price 6s. net.

VOLUMETRIC ANALYSIS. By H. P. STARCK. London: Baillière, Tindall & Cox. Price 7s. 6d.

SPIRIT TABLES TO BE USED WITH SIKES'S A AND B HYDROMETERS. H.M. Stationery Office. Price 2s. 6d. net.

THE LABORATORY: ITS PLACE IN THE MODERN WORLD. By D. STARK MURRAY. London: The Fenland Press. Price 2s.

THE DETECTION OF CRIME: AN INTRODUCTION TO SOME METHODS OF SCIENTIFIC AID IN CRIMINAL INVESTIGATION. By W. M. ELSE and J. M. GARROW. London: Office of *The Police Journal*. Price 6s. net.

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RAPID TESTING BY FLUORESCENCE. Slough: The British Hanovia Quartz Lamp Co., Ltd.

KINGSTON'S STERLING FLUCTUATION TABLES. (Rates of Exchange for Dollars, French, German, Swiss, Italian, Dutch, Czech, and Belgian currencies.) London: Kingston's Translation Institute, 96, Leadenhall Street. Price 1s. net.

TABLE INTERNATIONALE DES POIDS ATOMIQUES. Quatrième Rapport de la Commission des Poids Atomiques, 1934. Paris: Union Internationale de Chimie.

LE ACQUE MINERALI D'ITALIA. Direzione Generale della Sanità Pubblica. Rome.

REPORT OF THE BRITISH ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE, 1933.

MAY, 1934 Vol. 59, No. 698

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THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

An Ordinary Meeting of the Society was held at the Chemical Society's Rooms, Burlington House, on Wednesday, April 4th, the President, Mr. John Evans, F.I.C., being in the chair.

Certificates were read in favour of:—Frederick Frank Beach, M.A., B.Sc., F.I.C., Thomas Gifford Elliot, F.I.C., Frederick John Flowerdew, B.Sc., A.I.C., M.P.S., John Arthur Heald, M.C., B.Sc., F.I.C., Francis Edwin Needs, F.I.C., and Derrick John Saxby, B.Sc., A.I.C.

The following were elected members of the Society:—Ronald Andrew Balding, Bertram Eastwood Dixon, M.Sc., A.I.C., A.C.G.F.C., Arthur Glover, M.Sc., A.I.C., Ralph Gordon Harry, A.I.C., Reginald Milton, B.Sc., Roy Warren Watridge, B.Sc., F.I.C.

The following papers were read and discussed:—"The Determination of Small Quantities of Fluorides in Water," by Guy Barr, B.A., D.Sc., and A. L. Thorogood, B.Sc.; "A Test for Ethylene Glycol and its Application in the Presence of Glycerol," by A. W. Middleton, B.Sc., A.I.C.; and "The Detection of Diamines in Leather," by W. Mather, F.I.C., and W. J. Shanks.

NORTH OF ENGLAND SECTION

A meeting of the Section was held in Manchester on April 14th, 1934. The Chairman (Prof. W. H. Roberts) presided over an attendance of thirty-five.

The Chairman, on his own behalf and that of the members, congratulated Mr. J. Evans on his election as President of the Society.

The following papers were read and discussed:—"The Micro-Determination of the Molecular Weight of Volatile Liquid Compounds," by A. F. Colson, B.Sc., A.I.C.; "Note on the Determination of Chromium in the Presence of Iron, Aluminium and Phosphoric Acid," by J. Haslam, M.Sc., A.I.C., and W. Murray; "The Composition and Freezing-point of Colostrum," communicated by G. D. Elsdon, B.Sc., F.I.C.; and "The Technique of the Freezing-point Test for Milk," by G. D. Elsdon, B.Sc., F.I.C., and J. R. Stubbs, M.Sc., F.I.C.

Standards for Jam

THE Council has considered a letter received from the Food Manufacturers' Federation (Incorporated), relating to two matters connected with the standards and definitions for jam agreed upon by the Society and the Federation (ANALYST, 1930, 55, 694).

(i) The Committee of the Federation, having given consideration to the fact that certain members of the Federation have found it difficult to comply with the regulation in regard to size of type for the labelling of lower fruit standard jams, decided to suggest for the consideration of the Society that, in place of the present requirement, that the words "with other fruit juice" must be in letters of size equal to that of the name of the fruit or fruits, it should be permitted to use type of not less than half the size of that of the fruit name, with a minimum height of one-eighth inch. The minimum would apply in cases where the fruit name was printed in letters of quarter of an inch or less in height.

Examples: Strawberry (1 inch high)
With other fruit juice (½ inch high)
Strawberry (¼ inch high)
With other fruit juice (⅛ inch high).

In addition, of course, the label must bear the lower fruit standard as provided for in the regulations.

(ii) The Committee ruled that jams sold as "blackberry with apple jelly" should in future be described on the label as "blackberry and apple," and conform to the full fruit standard.

The Council of the Society has agreed to these alterations in the agreement.

Notes on a Semi-Quantitative Modification of the Elaidin Test

BY H. N. GRIFFITHS, PH.D., AND T. P. HILDITCH, D.SC., F.I.C.

(*Read at the Meeting of the North of England Section, February* 10, 1934)

THE well-known elaidin test, as first proposed by Poutet in 1819, for discriminating between non-drying and drying oils, consisted in shaking the fatty oil for three minutes with prescribed proportions of mercury and nitric acid, after which it was set aside for twenty minutes, and then again shaken for one minute. The relative hardness of the final product, and the time taken for this consistency to be attained, were observed and compared with the behaviour of various known oils under the same conditions of test. Various modifications of the test were proposed from time to time, and Archbutt (*J. Soc. Chem. Ind.*, 1886, 5, 303), after reviewing these suggestions, recommended the addition to the fatty oil (96 grms.) of a reagent (8 grms.) prepared by dissolving mercury (18 grms.) in nitric acid (15·6 ml.)

of sp.gr. 1·42; the mixture was placed in a wide-necked stoppered bottle immersed in water at about 25° C., and was shaken at intervals of ten minutes until solidification occurred. The length of time required for the fat to acquire a solid consistency, and the degree of solidity attained, were recorded by Archbutt for various oils. Non-drying oils, such as olive and almond oils, gave hard solid fats in two or three hours; mustard, neat's foot, and sometimes rape oil, gave butter-like products, and semi-drying oils, such as cotton-seed or sunflower-seed oils, were also observed to give products of a buttery or pasty texture; but linseed, hemp, walnut, and other drying oils remained quite liquid under the conditions of the test. Archbutt also records observations on the results obtained when the test was applied to olive oil mixed with certain other oils, from which it appears that he was able to detect the presence of 10 per cent. of rape or cotton-seed oil in olive oil from the consistence of the isomerised product and the time occupied in reaching the final consistence; poppy-seed oil had a marked effect, and could probably be detected in olive oil in proportions as low as 5 per cent., but the presence of 20 per cent. of "best nut oil" (? ground-nut oil) had little influence beyond somewhat prolonging the time taken to reach the final consistence, which was not quite so pronounced as in the case of the genuine olive oil.

We have lately been occupied with a quantitative investigation of the oleic-elaidic acid equilibrium and with an attempt to utilise this balanced reaction in the estimation of triolein in natural fats (*J. Chem. Soc.*, 1932, 2315). Although we were unable to achieve the latter object (owing to the low yield—30 per cent.—of trielaidin from triolein), we found that trielaidin could be separated from triolein by crystallisation from acetone under defined conditions; and that, consequently, within certain limits, a quantitative character could be given to the elaidin test as applied to fatty oils. Owing to changes in the nature of the oils used to adulterate olive oil, and to the development of improved alternative analytical procedures, the elaidin test is probably now of much less interest to the analyst than formerly. Nevertheless, it may be useful to record the proportions and characteristics of the crystallised "elaidins" obtained from a variety of oils under the standardised conditions which we are about to describe.

ISOMERISATION OF A FATTY OIL BY THE POUTET REAGENT.—We prefer to introduce the requisite quantities of mercury and nitric acid (sp.gr. 1·42) into the oil under examination, instead of preparing a stock solution of the reagent, as recommended by Archbutt.

The fatty oil (10 to 20 grms.), from which free fatty acids should be almost or entirely absent, is shaken with mercury (0·2 to 0·4 grm.) and nitric acid (0·5 to 1·0 ml.) in a stoppered bottle immersed in water at room temperature for one hour, and then left to stand overnight. The product, in solution in ether, is washed with dilute nitric acid to remove mercury compounds, and then with water until free from nitric acid. Ether and moisture are subsequently removed by evaporation, the residue being finally heated in a vacuum at 95° C. for a short time.

ISOLATION OF CRYSTALLINE GLYCERIDES FROM THE ISOMERISED OIL.—The dried product (5 grms.) is crystallised from acetone (20 ml.), the solution being kept at room temperature overnight and finally cooled at 0° C. for two hours. The separated crystals are collected and washed four times with acetone (5 ml. each time), dried in a vacuum desiccator, and weighed. The m.pt., iodine value and saponification value of the separated crystals are then determined.

Before describing the results obtained with various fatty oils, we may quote data which illustrate the application of the method to pure triolein and trielaidin.

DETERMINATION BY THE ABOVE PROCEDURE OF TRIELAIDIN IN MIXTURES CONTAINING KNOWN PROPORTIONS OF TRIOLEIN AND TRIELAIDIN.—Mixtures were made with synthesised triolein (iodine value 85·2) and synthesised trielaidin (m.pt. 42·8° C., iodine value 85·2, solubility in acetone at 0° C., 0·29 grm. in 100 ml.) in various proportions; these were submitted to crystallisation from acetone as described above, with the following results:

TABLE I

Trielaidin present, per cent.		100·0	78·6	61·2	39·4	19·6
Trielaidin isolated	per cent.	99·3	78·4	61·0	39·2	18·3
	m.pt., ° C.	42·3	42·1	42·2	42·0	42·3

ISOMERISATION OF SYNTHESISED TRIOLEIN.—The results of three typical experiments are given in the next table; crystallisation of the trielaidin was carried out, in each case, on 5 grms. of the isomerised glycerides.

TABLE II

Triolein used Grms.	Crystallised glycerides from acetone			Trielaidin Per Cent.
	Per Cent.	M.pt. ° C.	Iodine value	
18·0	32·6	40·5	81·4	31·1
9·4	26·7	40·5	82·9	26·3
8·8	28·5	41·5	83·4	28·0

The m.pt. of the crystallised product, which in each case was but little below that of trielaidin, was raised somewhat on admixture with the latter compound. We conclude, therefore, that di-elaido-mono-oleins do not separate under the conditions employed. The slight depression in m.pt., and the slightly low iodine values, are readily accounted for by the presence of traces of nitrogenous addition products which, as we have pointed out elsewhere (*loc. cit.*), are produced during the process of isomerisation.

APPLICATION OF THE PROCEDURE TO FATTY OILS.—We obtained, with a number of oils, the results summarised in Table III.

INTERPRETATION OF THE ANALYTICAL DATA.—It is essential to bear in mind, in considering the above figures, that the natural glycerides in vegetable fats are so built up that they contain, in general, minimum proportions of simple triglycerides. Hence an oil, such as olive or ground-nut oil, which was formerly supposed to consist very largely of triolein, is really made up of mixed glycerides in which, roughly speaking, one radical of acids present in much less amount than oleic acid (*e.g.* palmitic or linoleic acid) is linked with two oleic radicals in the glyceride molecule, and only the excess, so to speak, of oleic acid appears as simple triolein. Consequently, the "elaidins" do not consist, as would formerly have been supposed, of trielaidin, but of a mixture of the latter with the mono-saturated-dielaidins produced by isomerisation of some of the mono-saturated-dioleins originally present. Inspection of the iodine values of the crystallised "elaidins," given in the preceding table, illustrates this feature at once; the iodine value of the products is in all cases much lower than that of trielaidin (86·2).

TABLE III

Oil	Iodine value	Appearance of the elaidinised product	"Elaidins" crystallised from acetone			
			Per Cent.	M.pt. °C	Iod. val.	Sap. val.
Olive	84·9	Hard, solid mass	33·1	33·5	67·1	197·0
			35·5	37·0	68·8	196·1
Tea-seed	86·3	,, ,, ,,	38·8	36–37	73·0	193·2
			35·5	37–38	73·9	193·0
Almond	96·5	,, ,, ,,	29·3	39	79·5	191·3
			26·8	38·5	78·5	191·5
Ground-nut	90·5	Pasty mass	32·9	33	68·8	189·4
			31·8	35	65·9	189·9
Rape-seed	102·9	Butter-like mass	7·6	32	79·8	—
			7·9	32	79·3	184·0
Mustard-seed	104·0	,, ,, ,,	3·6	33	71·0	—
Cotton-seed	103·0	Semi-solid	1·3	—	45·4	—
			2·1	—	50·2	—
Soya-bean	129·6	Red liquid	Nil	—	—	—
Rubber-seed	136·2	,, ,,	Trace	—	—	—
Hemp-seed	166·3	,, ,,	Nil	—	—	—
Linseed	182·6	,, ,,	Nil	—	—	—

The mixed fatty acids of each oil submitted to the elaidin reaction during this work consisted of saturated, oleic, linoleic, linolenic, and erucic acids in the proportions given in Table IV. These data were obtained by the ester-fractionation method of analysis, supplemented (when linolenic acid was present) by thiocyanometric analysis; results by the latter process were also confirmed by estimation of oleic acid in the mixed fatty acids by means of the oleic-elaidic transformation, according to a procedure which we have recently described (*J. Soc. Chem. Ind.*, **1934, 53, 75** T; ANALYST, **1934, 363**). In Table IV the individual percentages of palmitic and other saturated acids have been omitted, since, for the purpose of the present discussion, the total proportion of saturated acids suffices.

It may be pointed out that, with the exception of olive oil (which contains 2 per cent. of tripalmitin; *cf.* Hilditch and Jones, *J. Chem. Soc.*, **1932, 805**), none of the oils examined contains any appreciable quantity of fully-saturated glycerides.

Olive, tea-seed and almond oils are the only instances, in the groups studied, in which it is likely that any substantial amount of triolein is present. In these oils, also, the ratio of saturated to unsaturated acids is sufficiently low to justify the supposition (in view of the present knowledge of glyceride structure in vegetable fats) that nearly all the saturated acids are combined in the form of mono-saturated-di-unsaturated glycerides. Further, since their contents of linoleic acid are relatively small, and since palmitic acid predominates in their saturated acids, the crystallised "elaidins" are probably made up almost wholly of mono-palmito-di-elaidins and tri-elaidin (with respective iodine values 59·2 and 86·2). If this is the case, the composition of the elaidins could be calculated approximately from their observed iodine values; but, unfortunately, our experience with trielaidin, isolated from pure triolein by the same procedure, shows that the iodine value of the product is usually somewhat low (82 to 83), and any estimate based on the observed iodine values would, therefore, be somewhat untrustworthy. The data for these three oils indicate, however, that something approaching half of the saturated acids present in the original fats has, in each case, been isolated in the form of mono-saturated-di-elaidins.

TABLE IV

Percentage of mixed fatty acids

	Saturated	Oleic	Linoleic	Linolenic	Erucic
Olive	12·7	79·8	7·5	—	—
Tea-seed	9·3	83·3	7·4	—	—
Almond	5·6	77·0	17·4	—	—
Ground-nut	17·7	60·4	21·9	—	—
Rape-seed	2	32	15	1	50
Mustard-seed	4	24·5	19·5	2	50
Cotton-seed	25·1	29·6	45·3	—	—
Soya-bean	13·4	26·1	54·7	5·8	—
Rubber-seed	18·4	23·6	43·3	14·7	—
Hemp-seed	8·6	6·7	68·8	15·9	—
Linseed	9·7	9·6	42·6	38·1	—

The case of ground-nut oil is complicated by the presence, on the one hand, of a higher relative proportion (22 per cent.) of linoleic acid in the mixed acids and, on the other, by that of saturated acids, in addition to palmitic acid, containing 18, 20, 22, and 24 carbon atoms in the molecule. Since ground-nut oil contains only about 60 per cent. of oleic acid, we are inclined to doubt, in view of the results with other oils, the presence of much triolein in the glycerides. Although the yield and iodine value of the ground-nut "elaidin" are not very different from those of olive or tea-seed "elaidins," we incline to believe that it does not represent the same type of material, but may be more complex in character and include, for example, glycerides containing arachidic and linoleic, in addition to elaidic acid. This is borne out, to some extent, by the marked difference in consistency between elaidinised ground-nut oil and elaidinised olive, tea-seed or almond oils. We hope, at a later date, to prepare elaidins from these four oils in sufficient quantity to permit us to make a more detailed study of their component acids.

Cotton-seed oil is interesting because the small quantity of elaidins produced has a relatively low iodine value. Here oleic acid forms only about 30 per cent. of the mixed acids, whilst the saturated acids (chiefly palmitic) amount to almost as great a proportion (25 per cent.). Triolein is almost certainly completely absent, and the low yield of elaidins evidently consists mainly of palmito-di-elaidin (iodine value 59·2), which is, however, accompanied by a certain amount of dipalmito-elaidin (iodine value 30·5).

Oils of the rape and mustard group also yield only small quantities of crystallised "elaidins"; from the very low contents (2 to 4 per cent.) of saturated acids in the original mixed acids, and the iodine and saponification values of the "elaidin," it would seem that the latter consists mainly, in this case, of mixed elaido-brassidins. It is, of course, possible, though *a priori* distinctly less likely, that the products are mixtures of trielaidin and tribrassidin.

Finally, in the four "drying" oils, oleic acid is definitely low in proportion to the remaining acids, and forms only from 6·7 to 26·1 per cent. of the mixed acids. No solid elaidins separate on isomerisation (except for a trace from rubber-seed oil, the acids of which contained 18·4 per cent. of saturated acids as well as 23·6 per cent. of oleic acid), and triolein is evidently not present; indeed, the oleic acid is almost certainly distributed in the glyceride molecules, so that, substantially, only mono-oleo-compounds occur in these oils (*cf.* for linseed oil, Eibner, Widenmayer and Schild, *Chem. Umschau*, 1927, **34**, 312).

UTILITY OF THE ELAIDIN REACTION IN DETECTING ADULTERATION OF OLIVE OIL.—Since the chief analytical interest of the elaidin test lies in its possible application in the examination of olive oils, it may be well to consider how far the amended procedure suggested in this paper is likely to be of assistance in this direction. It does not appear very serviceable, at the outset, in the detection of tea-seed oil in admixture with olive oil, although the crystallised elaidin of tea-seed oil has a definitely higher iodine value and slightly lower saponification value than that from olive oil; the differences are not sufficient, however, to permit of the method being employed with much success in this instance. It is remarkable how closely olive and tea-seed oils resemble each other in their fatty-acid composition and also in their glyceride structure; the only significant difference is that the fruit-flesh olive oil contains a very small proportion (2 per cent.) of tripalmitin. This feature, although evident as a result of complete oxidation of large quantities of oil, does not lend itself to use as an analytical means of identification. Apparently, differentiation between the two oils must be sought in the characteristics of their non-fatty components—for example, the iodine values of the unsaponifiable matter (Bolton and Williams, ANALYST, 1930, **55**, 5).

Almond oil, in consequence of its low saturated acid content, yields an elaidin which resembles trielaidin in iodine and saponification values more nearly than that of either olive or tea-seed oil; in consequence, the proportion of elaidin from almond oil is several per cent. lower than in the latter two oils, whilst its melting-point is definitely higher (38 to 39°). The yield of elaidin from ground-nut oil is intermediate between those of the products from olive and almond oil, and its iodine value is little different from that of olive-oil elaidin, but its saponification value is definitely lower (189 to 190, as compared with 196 to 197), its m.pt. is somewhat lower, and its consistence is less brittle.

The proportions of elaidins produced from the remaining oils (*cf.* Table III) are small or negligible, so that the presence of these oils in any quantity in a reputed olive oil would be clearly indicated by a pronounced decline in the total yield of crystallised elaidins. In these circumstances, also (except in presence of added rape or mustard-seed, and possibly cotton-seed, oils), the m.pt., iodine and saponification values observed would be those of the olive oil elaidin. Rape and mustard-seed oil would be expected, in addition to causing a decreased yield of elaidin, to have a depressant effect on its melting-point, the iodine value of which would be somewhat increased, whilst its saponification value would be low in comparison with the corresponding figures for olive oil elaidin. Cotton-seed oil, if present in some quantity, would cause a fall in both the yield and the iodine value of the crystallised elaidin.

Deviations from the average values of the crystallised olive oil elaidin in the directions indicated in Table V might be accepted as indications of the probable presence, in a specimen of olive oil, of other oils as follows:

TABLE V

"Elaidins" crystallised from acetone				Oil suspected
Yield (on oil) Per Cent.	M.pt. °C.	Iod. value	Sap. value	
33–35	34–37	67–69	196–197	(Genuine olive oil).
Same	36–38	Slightly higher	Slightly lower	(?) Tea-seed.
Lower, but not less than 30 per cent.	Not lower	Somewhat higher	Between 196 and 190	Almond (possibly rape or mustard in small proportions).
,, ,, ,,	Somewhat lower	As for olive	Lower than for olive	Ground-nut.
,, ,, ,,	As for olive	As for olive	As for olive	Semi-drying or drying oils (up to about 20 per cent. of the original oil).
Below 30 per cent.	Somewhat lower	Higher	Low	Rape, mustard-seed (over 20 per cent. of the original oil).
,, ,, ,,	As for olive	As for olive	As for olive	Semi-drying (*e.g.* cotton-seed) or drying oils (over 20 per cent. of the original oil).

We desire to thank Messrs. Lever Brothers, Ltd., whose Research Studentship in this laboratory was held by one of us (H. N. G.) during the course of this work.

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Quantitative Determination of Acetone and Ethyl, Butyl and Iso-Propyl Alcohols in Fermentation Liquors

G. L. STAHLY, O. L. OSBURN AND C. H. WERKMAN

THE differential distribution of the fatty acids between two immiscible solvents is employed in the partition method described by Werkman (*Ind. Eng. Chem., Anal. Ed.*, 1930, 2, 302) for the quantitative determination of the acids in a mixture. The partition method is adapted in the present communication to the quantitative determination of mixtures of acetone and ethyl, butyl and iso-propyl alcohols, or any combination of these. A need for such a method is felt in investigations involving the butyl-acetonic fermentation.

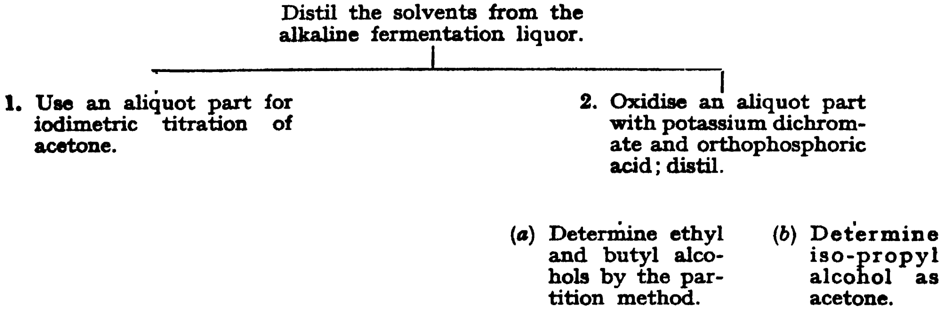
In the present procedure a neutral or slightly alkaline aliquot portion of the fermentation liquor is distilled directly. Acetone is determined in an aliquot part of the distillate by a modification of Messinger's method, as described by Goodwin (*J. Amer. Chem. Soc.*, 1920, 42, 39). The alcohols are then oxidised in a second aliquot part of the distillate without removing the acetone. Ethyl alcohol is oxidised to acetic acid, whilst 89·6 per cent. of the butyl alcohol is oxidised to butyric acid and 10·4 per cent. to acetic acid. These values agree with those obtained by van der Lek (*Onderzoekingen over de Butyl-Alkoholgisting*, Thesis, Delft, 1930) and Werkman and Osburn (*Ind. Eng. Chem., Anal. Ed.*, 1931, 3, 387). It was found that 94 per cent. of the iso-propyl alcohol is oxidised to acetone. The oxidised mixture, containing butyric and acetic acids and acetone, is distilled. The acetone in the distillate is determined iodimetrically, and the acids are determined by the partition method. By a simple calculation of the partition coefficient, the percentages of ethyl and butyl alcohols can be read directly from a nomogram (Fig. 3).

Van der Lek, working with similar mixtures, determined acetone by precipitation with 2, 4-dinitrophenyl hydrazine. The alcohols were oxidised with potassium dichromate and sulphuric acid at two different temperatures. The acids were steam-distilled and quantitatively determined by the method of Duclaux. The iso-propyl alcohol was oxidised to acetone and determined in the same manner as the acetone in the original mixture. Van der Lek's method requires considerably more time than the method described in this paper.

Adams and Nicholls (ANALYST, 1929, 54, 2) quantitatively analysed mixtures of acetone, ethyl alcohol, and iso-propyl alcohol. They oxidised the mixture with potassium dichromate and sulphuric acid at room temperature. The acetone and acetic acid resulting were steam distilled, the acid was titrated, and the acetone was distilled and determined by specific gravity or colorimetrically.

PROCEDURE.—The procedure we have followed is outlined in Fig. 1. The alcohols and acetone are distilled from 500 ml. of the neutral or slightly alkaline fermentation liquor by direct distillation. If the mixture froths much, distillation can be carried out from slightly acid solution; about 250 ml. of the distillate thus collected are neutralised and re-distilled. The second distillate is brought to a volume of 200 ml. and 50 ml. of it are placed in a 200-ml. balloon flask containing 10 grms. of potassium dichromate and 25 ml. of 85 per cent. orthophosphoric acid. The flask is connected at once with an efficient reflux condenser and crushed ice is placed in the upper portion of the condenser tube. A few glass beads or pieces of porcelain are used to prevent bumping. The mixture is heated so that boiling starts after two minutes, and gentle boiling is continued for six minutes. During the heating the condenser tube is rinsed once or twice with small portions of carbon dioxide-free water. The flask, with the condenser still attached, is then cooled rapidly by immersing in cold water. The condenser tube is again rinsed into the flask. The latter is removed, and quickly connected with a Liebig condenser, and the mixture is distilled into an iced receiver. The outlet tube leading from the flask to the condenser should be of fairly large bore, to prevent any liquid from being mechanically forced over into the distillate. There is no tendency to bump and the distillation proceeds smoothly. Frothing, which occurs near the end of the process, is maintained for two or three minutes until the froth nearly, but not quite, fills the flask. All the acetone and organic acids are distilled. Phosphoric acid has not been found to distil over in significant quantities. As soon as the foam has subsided, the distillation flask is removed and the stopper and end of the outlet tube are rinsed to remove any oxidising reagents. The condenser tube is then rinsed, and the water is collected in the receiver containing the distillate, which should be colourless. The volume is made up to 200 ml. with carbon dioxide-free water, and aliquot portions are taken for the different analyses, the determinations being carried out as follows:—

OUTLINE OF ANALYSIS



Distil the solvents from the alkaline fermentation liquor.

1. Use an aliquot part for iodimetric titration of acetone.

2. Oxidise an aliquot part with potassium dichromate and orthophosphoric acid; distil.

(a) Determine ethyl and butyl alcohols by the partition method.

(b) Determine iso-propyl alcohol as acetone.

FIG. 1.

DETERMINATION OF ACETONE.—Acetone is determined quantitatively in an aliquot part of the distillate by a modification of Messinger's method, as described by Goodwin (*J. Amer. Chem. Soc.*, 1920, **42**, 39) (Fig. 1).

A temperature of approximately 0° C. is maintained, and the iodine is allowed to react for 10 minutes before acid is added and the iodine back-titrated. Under these conditions the acetone reacts completely with the iodine, whereas the ethyl and iso-propyl alcohols do not react. Table I gives the results of typical analyses.

TABLE I

QUANTITATIVE DETERMINATION OF ACETONE

Mixture	Contained ml.	Acetone found ml.		
1. Acetone	1·30	1·31	1·30	1·30
2. Acetone	1·30	1·30	1·29	
Ethyl alcohol	2·50			
3. Acetone	1·235	1·235	1·235	
Iso-propyl alcohol	2·50			

All solutions are one-tenth molar.

DETERMINATION OF ISO-PROPYL ALCOHOL.—Iso-propyl alcohol is oxidised to acetone and determined iodimetrically in the distillate. In a series of trials with iso-propyl alcohol alone the following percentages were recovered as acetone:—95·3, 94·7, 93·6, 92·8, 93·0, an average recovery of 93·9 per cent. Iso-propyl alcohol in mixtures with butyl and ethyl alcohols gave substantially the same results. Likewise, when acetone alone was subjected to routine oxidation and distillation, 94 per cent. was recovered. These results indicate that the loss of 6 per cent. occurs after the iso-propyl alcohol has been oxidised to acetone. To find the quantity of iso-propyl alcohol, therefore, divide the total acetone after oxidation by 0·94, and subtract the acetone present in the original sample.

Neither mixtures of iso-propyl and butyl alcohols, nor those of acetone and butyl alcohols gave higher yields of acetic acid than did butyl alcohol alone, so that failure to recover 100 per cent. of the acetone is apparently not due to oxidation to acetic acid.

DETERMINATION OF ETHYL AND BUTYL ALCOHOLS.—Sixty ml. of the distillate, which should be approximately 0·03 N acid, are shaken vigorously for one minute in a separating funnel with 25 ml. of acid-free anhydrous diethyl ether at 25° C. After three minutes 50 ml. of the aqueous phase are withdrawn and titrated with standard sodium hydroxide solution, phenolphthalein being used as indicator. The number of ml. of sodium hydroxide solution required is recorded as P'. Fifty ml. of the unpartitioned distillate are titrated, and the number of ml. required is recorded as M. Then $P'/M \times 100 = K$. This value, K, is designated the percentage partition constant for the acid solution.

In Fig. 2, the values of K are plotted against the percentages of acetic and butyric acids. The graph was drawn by finding the values of K, as just explained, for various known mixtures of pure acetic and butyric acids. Therefore, after K has been computed for any mixture of acetic and butyric acids, the percentage composition on a molar basis can be read directly from the graph. The partition constant for pure acetic acid is 83·3; that for pure butyric acid 34·5.

In order to convert K into percentage of ethyl and butyl alcohol, it is first necessary to determine the behaviour of these alcohols under our conditions of oxidative treatment. Ethyl alcohol, after oxidation, gave the same value for K as did pure acetic acid, indicating acetic acid to be the only acid produced. Butyl alcohol gave a mixture of butyric and acetic acids. Under the conditions of

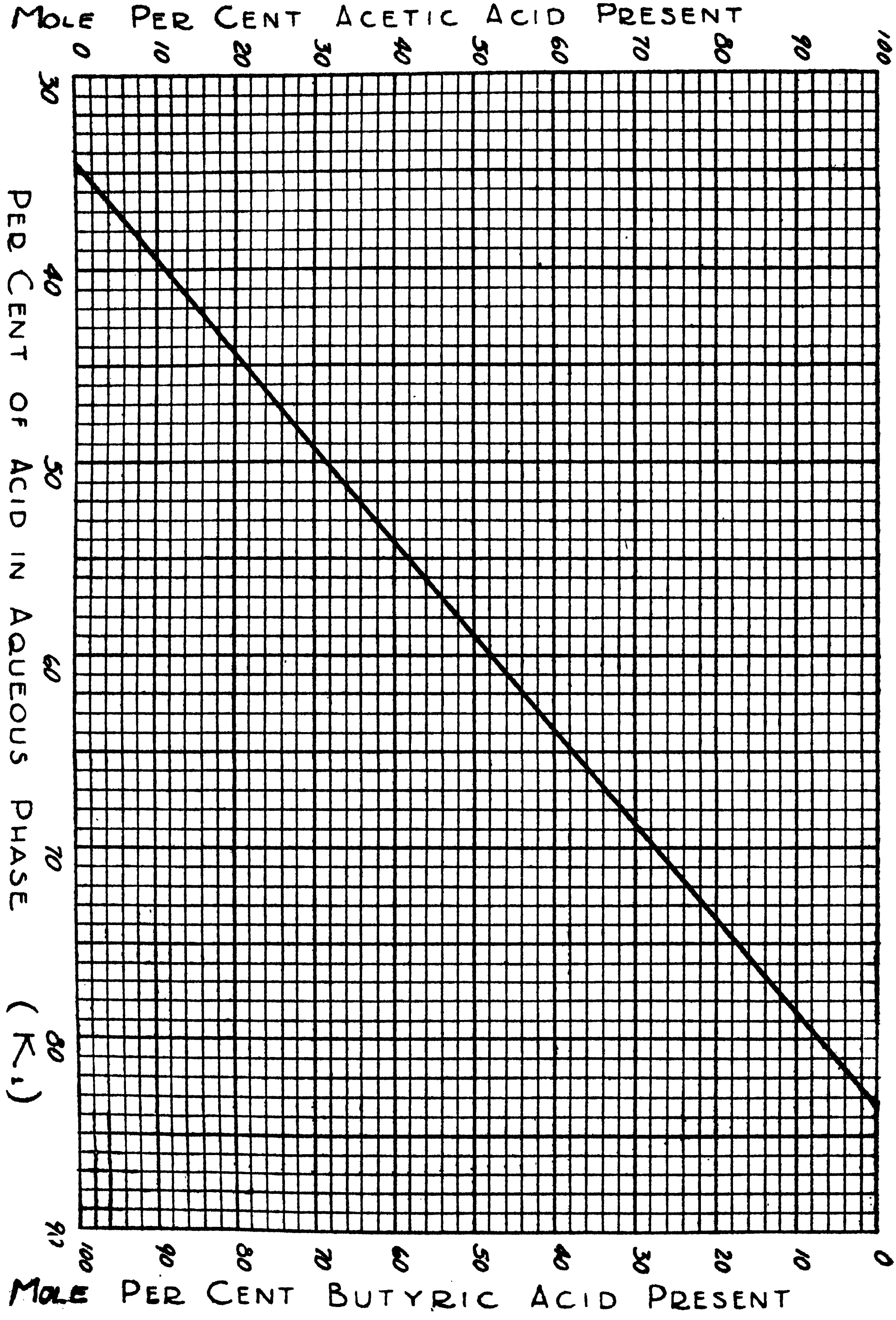

Mole Per Cent Acetic Acid Present
0
10
20
30
40
50
60
70
80
90
100
30
40
50
60
70
80
90
Per Cent of Acid in Aqueous Phase (K₁)
100
90
80
70
60
50
40
30
20
10
0
Mole Per Cent Butyric Acid Present

Fig. 2.

oxidation used in these tests, an average of 89·6 per cent. of butyric acid was produced. In order to arrive at this value for butyric acid, solutions of butyl alcohol were oxidised, and their partition constants were computed. By using these constants in Fig. 2 the percentages of butyric acid can be read directly. The values obtained were: 89·8, 89·0, 90·0, 89·6, and 89·6 per cent. of butyric acid. No formic or propionic acid could be detected. The average percentage of the butyl alcohol recovered as acids was 98·2 per cent., assuming that one mole of alcohol yields one mole of acids.

It is convenient to construct a diagram from which the percentage of each alcohol may be read directly. This is done by determining the partition constants for the oxidised products of pure butyl alcohol (39·2) and ethyl alcohol (83·3) and various known mixtures of them. These values of K are plotted in Fig. 3 against the molar percentages of the alcohols.

An example will make clear the use of Fig. 3. An unknown mixture of ethyl and butyl alcohols, after oxidation, gave a partition constant of 60. From Fig. 3 it is seen that if K = 60, the alcohols in the mixture must be 47·0 mole per cent. of ethyl alcohol and 53·0 mole per cent. of butyl alcohol. From the amount of total acids present the concentrations of each alcohol in the mixture can be readily computed.

The partition constant obtained with mixtures of acetic and butyric acids was not affected by the presence of acetone in the concentrations used in these experiments.

Results obtained by using these methods on known mixtures of acetone and the alcohols are recorded in Table II. Compounds of a high degree of purity were twice distilled, and the middle fraction of constant boiling-point was used. All volumes are expressed as ml. of 0·1 molar solutions.

TABLE II

QUANTITATIVE DETERMINATION OF MIXTURES OF ACETONE AND ALCOHOLS

Mixture	Contained ml.	Found ml.	Per cent. of original found
1. Acetone	13·0	13·12	101·0
Iso-propyl alcohol	50·0	49·8	99·6
Ethyl alcohol	50·0	49·0	98·0
Butyl alcohol	100·0	99·5	99·5
2. Acetone	10·4	10·49	100·8
Iso-propyl alcohol	40·0	41·1	102·7
Ethyl alcohol	18·8	18·3	97·2
Butyl alcohol	100·0	101·3	101·3
3. Ethyl alcohol	50·0	50·9	101·8
Butyl alcohol	200·0	191·5	96·0

All solutions are one-tenth molar.

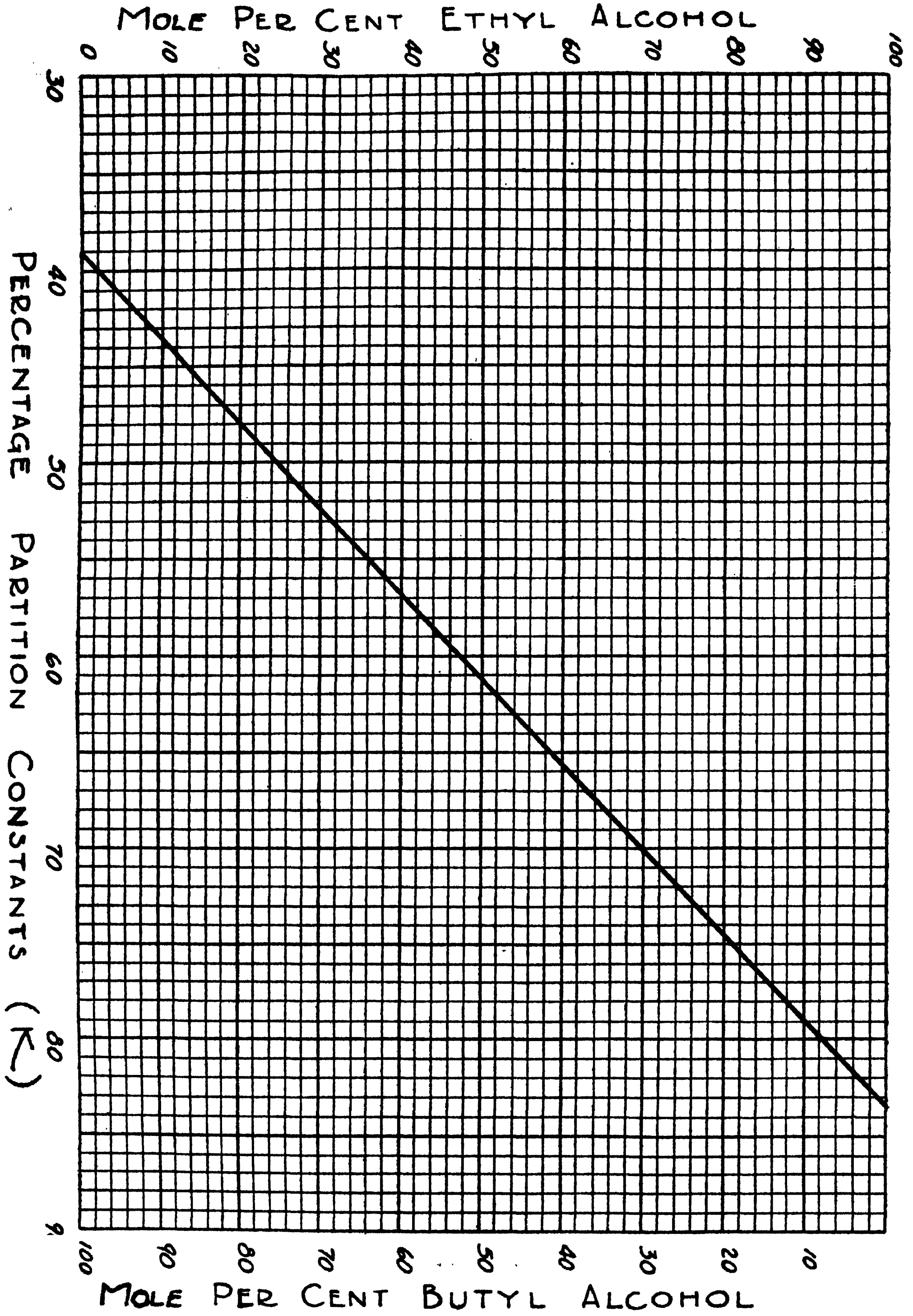

MOLE PER CENT ETHYL ALCOHOL
0
10
20
30
40
50
60
70
80
90
100
PERCENTAGE PARTITION CONSTANTS (K)
30
40
50
60
70
80
90
100
90
80
70
60
50
40
30
20
10
MOLE PER CENT BUTYL ALCOHOL

Fig. 3.

DISCUSSION.—The procedure outlined should be followed in detail. The concentration of the phosphoric acid should be constant, since any change causes a small shift in the ratio of acetic to butyric acid originating from the butyl alcohol. The manner of heating the mixture may also cause variation in the acid ratio. Care must be taken to prevent loss of the more volatile compounds during each stage of the heating process. Likewise, the condensers must be well rinsed with water free from carbon dioxide at the close of each process. The temperature of the partition mixture should not vary by more than ±2° from 25° C. The ether used must be anhydrous and free from acids.

The method here described is accurate for solutions which contain from 0·02 to 0·05 *N* acid after oxidation. The partition constants for the acids shift slightly as the acid solutions vary in concentration. If it is necessary to work with other concentrations, new constants should be established to fit the conditions.

The method of analysis outlined in this paper is accurate, convenient, and rapid. The complete analysis, starting with the neutral solvents, can be carried out in about one hour.

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The Volumetric Determination of 8-Hydroxyquinoline

BY H. RONALD FLECK, F. J. GREENANE AND A. M. WARD, D.Sc., F.I.C.

DURING studies on the volumetric determinations of metals, by titrating hydrochloric acid solutions of the metallic complexes of 8-hydroxyquinoline, we have obtained indefinite and variable end-points in a number of cases. This variation is well illustrated by the results shown in the following table, in which Column 1 gives the volumes taken of a solution in *N* acetic acid of 8-hydroxyquinoline (A.R.) (20·500 grms. per litre, *i.e.* 1 ml. ≡ 5·655 ml. of *N*/10-$KBrO_3$, assuming bromination to proceed according to the equation:—$C_9H_7ON + 2Br_2 \rightarrow C_9H_5ONBr_2 + 2HBr$). In all cases, 20 ml. of concentrated hydrochloric acid (approx. 12 *N*) were present, and the solution, contained in a stoppered bottle, was made up to 100 ml. with water. The volumes of *N*/10 potassium bromate solution (2·784 grms. of $KBrO_3$ and 12 grms. of KBr per litre), shown in Column 2, were then added, the solutions were allowed to stand for 5 minutes, 10 ml. of 10 per cent. potassium iodide solution were introduced, followed by starch solution, and the liberated iodine was titrated with *N*/10 sodium thiosulphate (Column 3). The results of independent duplicate determinations are shown.

Oxine solution ml.	$N/10$ $KBrO_3$ added ml.	$N/10$ $Na_2S_2O_3$ ml.	$N/10$ $KBrO_3$ used ml.	Calc. titre ml.
10·0	60·0	3·02, 3·15	56·98, 56·85	56·55
9·0	55·0	3·65, 3·89	51·35, 51·11	50·90
8·0	50·0	3·32, 4·04	46·68, 45·96	45·24
7·0	50·0	9·38, 7·88	40·62, 42·12	39·59
7·0	48·0	8·03, 6·26	39·97, 41·74	39·59
7·0	45·0	4·87, 4·33	40·13, 40·67	39·59
7·0	42·0	1·97, 2·12	40·03, 39·88	39·59
6·0	40·0	6·10, 4·63	33·90, 35·37	33·93

In these experiments, except in one case, when 6·0 ml. of oxine were used, the end-points were unsatisfactory. In those cases in which inexact end-points were obtained, a brown cloudiness developed during addition of the potassium iodide. If the solution cleared during the thiosulphate titration, the starch-iodide colour did not return after standing, but if a slate-blue solid was present at the end of the titration, the starch-iodide colour could be seen to return from this to the bulk of the liquid. Even when the titrations were carried out with vigorous shaking, the end-points were still unstable. It would appear that, in the unsatisfactory experiments, a part of the dibromo-oxine separated from solution, after addition of potassium iodide, possibly as a polyiodide, or the solid might be an adsorption complex of iodine and dibromo-oxine. Whatever the nature of the solid, the difficulty was completely avoided by adding carbon disulphide to the solution before adding potassium iodide, as follows:—

To the oxine solution in a stoppered bottle were added 20 ml. of concentrated hydrochloric acid, and the volume was made up to 100 ml. with water. Potassium bromate solution ($N/10$) was added in a fine stream, with swirling, until excess of bromine was present, as shown by removing a drop of the liquid and testing with starch-iodide paper (Bright and Fowler, *Bur. of Standards J. Research*, 1933, **10**, 333). After standing for 5 minutes the liquid was again tested to ensure that bromine was in excess, and 15 ml. of carbon disulphide were introduced. The mixture was shaken and bromine then passed mainly to the carbon disulphide layer. Ten ml. of 10 per cent. potassium iodide solution were added slowly, with shaking. A brown colour sometimes appeared at first, but rapidly changed to violet. Titration with $N/10$ sodium thiosulphate solution was then carried out, with shaking and addition of starch solution towards the end of the titration, until the colour of the aqueous layer changed sharply to a bright yellow-green tint. The end-points were permanent for at least an hour, the solid present at the end of the reactions had a pale brown silky appearance, and the carbon disulphide solution was not colourless, but pale brown.

Oxine soln. ml.	$N/10$ $KBrO_3$ ml.	$N/10$ $Na_2S_2O_3$ ml.	Titre ml.	Calc. titre ml.
10·0	59·10	2·28	56·82	56·55
8·0	48·00	2·62	45·38	45·24
7·0	41·00	1·43	39·57	39·59
4·0	23·50	0·90	22·60	22·62
2·0	12·10	0·74	11·36	11·31
1·0	6·15	0·47	5·68	5·65
0·5	3·00	0·19	2·81	2·82

The following experiments were made by the procedure with carbon disulphide described above, to establish (*a*) the time necessary for complete bromination, (*b*) the effect on the end-point of the excess of bromate used, and (*c*) the effect of varying the concentration of hydrochloric acid. The results given are the mean of two independent sets of observations, except when the values did not justify a mean being taken; both results are then given.

(*a*) Five ml. of oxine solution (≡ 28·28 ml. of $N/10$ $KBrO_3$); 20 ml. of concentrated hydrochloric acid; 75 ml. of water; 30·00 ml. of $N/10$ $KBrO_3$ were added in a fine stream; about 1 minute was required for the addition. The times of standing, after addition of the potassium bromate, are shown, and also the amount of $N/10$ potassium bromate consumed, based on the back titre with sodium thiosulphate.

Time: minutes	20	10	5	2	0
Titre: ml.	28·27	28·23	28·29	28·26	28·04

(*b*) Amounts of oxine, acid, and water as in (*a*).

Vol. of $KBrO_3$ added: ml.	28·70	28·70	28·70	28·70	35·00	35·00
Time of standing: minutes	10	5	2	0	10	5
Vol. of $KBrO_3$ consumed: ml.	28·22	28·23	28·18	28·15	28·33	28·35

(*c*) Oxine solution, 5 ml.; varying quantities of concentrated hydrochloric acid; water to total volume of 100 ml.; 30·00 ml. of $N/10$ $KBrO_3$ added, and titrated after 5 minutes' standing.

Conc. HCl: ml.	50	40	30	10	5	2	1
Vol. of $KBrO_3$ consumed: ml.	27·96 28·37	28·06 28·52	28·05 28·27	28·32	28·26	16·20 14·04	12·78 11·73

In the experiments in which 10 ml. or less of hydrochloric acid were used crystals separated during the bromination. When 2 ml. or 1 ml. of hydrochloric acid were used it was not possible, after adding carbon disulphide and shaking, to see the colour of bromine in the carbon disulphide layer. On the addition of potassium iodide a pale colour, due to iodine, developed, and this increased during the titration with sodium thiosulphate until a maximum was attained; the colour then gradually decreased, until a very unstable end-point was reached.

The experiments described under (*a*), (*b*) and (*c*) were repeated with 5 minutes' standing, but without adding carbon disulphide. The results were substantially the same as when carbon disulphide was present, except that the end-points were sluggish and in (*b*) for experiments in which 35·00 ml. of $N/10$ potassium bromate solution were used, a blue solid was present after the starch-iodide colour was removed from the aqueous solution; the end-point was unstable, and the blue colour returned to the solution from the solid contained in the liquid.

Provided, therefore, that the concentration of oxine was such that, during the addition of potassium iodide, material did not separate and remain after the titration, the end-points were as satisfactory in the absence of carbon disulphide as in its presence; whatever conditions were chosen, however, provided the acid concentration was suitable, the procedure described, with carbon disulphide present, gave very sharp, exact and permanent end-points. Similar experiments in the presence of carbon disulphide, made on a number of metallic complexes of the reagent, have given equally good results.

Attempts were made to replace carbon disulphide by chloroform or carbon tetrachloride, but in each case the slate-blue solid was formed and did not dissolve (or dissolved very slowly), and the end-points were therefore inexact. In the procedure with carbon disulphide the slate-blue solid does not appear, possibly because the adsorption complex (or polyiodide) is much more soluble in that solvent than in the others.

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Simplifications in the Method of Separation of Metals by Graded Potential

BY A. J. LINDSEY, M.SC., A.I.C., AND H. J. S. SAND, D.SC., PH.D., F.I.C.[*]

A CONSIDERABLE simplification of the electrolytic separation of metals by graded potential was introduced by Lassieur,[†] who replaced the potentiometer for the measurement of the potential difference between the auxiliary electrode and the cathode by a combination of a galvanometer and series-resistance of 26,000 ohms, which he used as an ordinary voltmeter.

Lassieur recognised that his voltage measurements were not correct, but, being repeatable, they were sufficiently accurate for his purposes. They are open to the obvious criticism that different workers using auxiliary electrodes of different resistances must employ different voltage readings. The following investigation was undertaken to determine the magnitude of the errors in Lassieur's voltages, and to make suggestions for such modifications of the method as would allow it to be more generally applied. The possible causes of error are:

1. Polarisation of the auxiliary electrode due to the current taken from it by the galvanometer.

2. The back-resistance of the auxiliary electrode. If the resistance of the auxiliary electrode is a, that of the galvanometer plus series-resistance g, the voltage read v, and the correct voltage e, then,

$$\frac{e}{v} = \frac{a+g}{g} \text{ or } e = v + \frac{va}{g} \quad \ldots\ldots\ldots\ldots \quad (1)$$

The relative correction is thus a/g.

THE AUXILIARY ELECTRODE.—Lassieur employs a simplified $N/1$ calomel electrode consisting of $N/1$ potassium chloride solution in contact with mercury, the usual mercurous chloride being omitted. A certain amount of calomel will undoubtedly always form on the surface of the mercury in such an electrode, so that it will represent an approximation to a normal calomel electrode. In Lassieur's technique it is obviously desirable that the auxiliary electrode should have as low a resistance as possible. The electrode vessel previously described by one of us (ANALYST, 1929, **54**, 282) was modified with this end in view. It is shown in Fig. 1. The internal cross-section of the connecting arm has remained at about 4 mm., but the contracted bends, designed to prevent diffusion of the test liquid into the auxiliary electrode, have been replaced by bends of the shape shown that are not contracted. Of these, the double bend *a* (*vide* figure) is placed mainly outside the test solution, whereas the small single bend *b* is inside it. The position of the reservoir funnel *R* has also been altered. It is now placed on the connecting arm, so that there is no chance of carrying liquid from the electrode-vessel into the test solution when the connecting liquid is being flushed out. The bracket for holding the electrode-vessel, which used to consist of a single adjustable arm, has now been replaced by the double-arm bracket shown in the figure. Much more ready adjustment is thus obtained. The electrode illustrated is fitted with a connecting wire for mercury, which may obviously be omitted when a platinum foil for use with quinhydrone is attached to the rubber stopper, as shown at *F*. Several different auxiliary electrodes, including Lassieur's potassium chloride electrode, fitted both without and with the filter-paper plug recommended by him, were made up and tested for polarisability and resistance. Their potential differences against a saturated calomel electrode were also determined.

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[*] NOTE. The experiments described in this paper were carried out by the former author, whereas the apparatus was designed by the latter.

[†] A. Lassieur, *Compt. rend.*, 1923, **177**, 1114; 1924, **178**, 847; 1924, **179**, 632; 1924, **179**, 847. *Bull. Soc. Chim.*, 1924, [iv], **39**, 1530. *Ann. Chim.*, 1925, [x], **3**, 235. *Bull. Soc. Chim.*, 1925, [iv], **39**, 1167. *Electro-analyse Rapide* (Paris, 1927).

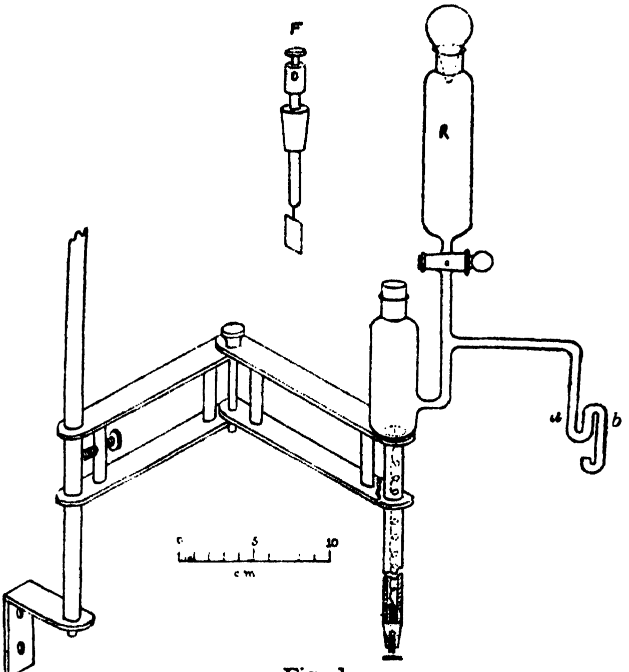

Fig. 1.

The electrodes were:

TABLE I

MERCURY ELECTRODES

A	Hg | Hg_2Cl_2 | KCl. (*N*/1) |
B	Hg | Hg_2Cl_2 | KCl. (saturated) |
C	Hg | Hg_2Cl_2 | KCl. (solid) | $NaNO_3$. (50 grms./100 ml.) |
D	Hg | Hg_2Cl_2 | KCl. (solid) | $Na_2SO_4.10H_2O$. (20 grms./100 ml.)
E	Hg | Hg_2SO_4| H_2SO_4. (2 *N*) |
F	Lassieur's electrode (*op. cit.*, p. 58). Hg | KCl. (*N*/1)[1]

TABLE II

QUINHYDRONE ELECTRODES

G	Pt | acid KCl solution, saturated with quinhydrone
H	Pt acid $NaNO_3$ solution,
I	Pt H_2SO_4 (*N*/1)
J	Pt HCl (*N*/1)

All electrodes except F were set up in the vessel shown in Fig. 1. Solution G contained 25 grms. of potassium chloride and 1 ml. of *N*/1 hydrochloric acid per 100 ml. of solution, and solution H contained 50 grms. of sodium nitrate and 1 ml. of *N*/1 nitric acid per 100 ml. of solution.

TABLE III

Electrode		Polarisation (millivolts) after			
		½ hour	1 hour	1½ hours	2 hours
A	+	3	3	3	3
	−	2	3	2	2
B	+	1	1	1	1
	−	1	2	1	2
C	+	0	1	0	0
	−	0	1	0	2
D	+	0	0	0	0
	−	0	0	0	0
E	+	1	0	2	1
	−	0	1	2	2
F	+	25	82	109	122
	−	17	23	23	24
G	+	1	3	3	5
	−	5	7	8	8
H	+	6	9	8	9
	−	0	1	4	5
I	+	0	5	5	9
	−	0	0	2	2
J	+	0	0	0	0
	−	1	1	1	0

The polarisation of these electrodes was tested when a current of 20 microamperes (corresponding to a reading of one volt on our 50,000 ohms voltmeter) was passing through them for varying periods in both directions. Their potentials against a saturated calomel electrode were measured by a potentiometer. In Table III the variations representing polarisations after the times stated are given in millivolts. The sign + indicates that the polarising current was leaving, the sign — that it was entering the electrode under test. The former case is the usual one in metal separations.

It will be seen that Lassieur's potassium chloride - mercury electrode is subject to great polarisation, and we do not recommend it for use as an auxiliary electrode during quantitative depositions. The polarisation of the mercurous salt - mercury electrodes is small and almost constant, and their use is recommended for the control of cathode potential.

The polarisation figures also show that the quinhydrone electrodes are suitable for auxiliary electrodes, but, as will be seen later, their resistances are variable and high, and on this account they are not suitable for Lassieur's high-resistance voltmeter technique. In connection with the polarisation of these quinhydrone electrodes it should be noted that, although the values after two hours are somewhat high, the original value may in every case be regained (within one or two millivolts) by rocking the platinum electrode in the solution.* The figures quoted are those obtained by measurement of the potential after the electrode and solution had remained perfectly quiescent for the period stated.

ELIMINATION OF THE ERROR DUE TO THE BACK RESISTANCE OF THE AUXILIARY ELECTRODE.—The galvanometer we have used as a voltmeter is a pointer instrument of the unipivot type of a little under 1000 ohms internal resistance, marketed as type L by the Cambridge Scientific Instrument Company. We have had it fitted with a series-resistance so as to give a full-scale reading on a mirror-backed scale at 1·2 volts. It is calibrated in centivolts so that millivolts may be estimated with fair accuracy. The total resistance is 50,000 ohms, and the series-resistance may be short-circuited by means of a shunt actuated by a button. It will be seen that the instrument will detect a current of about 0·02 micro-ampere (corresponding to 1 millivolt), and can therefore be used as a detecting galvanometer for many purposes. It was thought not only that an instrument of this type could be used as a voltmeter for routine work in Lassieur's technique, but also that it might be possible to design a simple potentiometer assembly of the voltmeter-potentiometer type (Tafel, *Z. physikal. Chem.*, 1905, **50**, 662; Sand, *J. Chem. Soc.*, 1907, **91**, 380), constructed mainly of wireless fittings to which our voltmeter could be attached and, at the will of the operator, either play the part of an independent direct-reading instrument, or be used as part of the potentiometer first in the capacity of a zero instrument, and then in that of a voltmeter. Fig. 2 (omitting the dotted portion) shows the wiring diagram adopted, and Fig. 3 gives a view of the completed box, including the dry cell, as constructed for us by Messrs. Griffin & Tatlock.

The assembly has four terminals, two of which (marked "voltmeter," Fig. 2) are connected with our instrument, the other two (marked X) being joined to the points to be controlled. The battery is first put in circuit by pulling out the push-pull switch. The latter is arranged so that to close the box the switch must be off. If it is desired to know the reading of the voltmeter when connected directly with the points X, the double pole throw-over switch A is first put in the position "To direct." It is then altered to the "To potentiometer" position. The voltmeter now acts as a zero instrument between the coarse-adjustment slider S_c and the point X_+. In order that it should give a positive reading, the zero point of S_c should be at the extreme + end of the potentiometer. S_c is then moved until the voltmeter registers zero. The fine adjustment is then completed by means of the fine adjustment slider S_f, the button for cutting out the back resistance of the voltmeter being depressed. This button is then released and the morse-key M depressed. The voltmeter then registers the P.D. between the points S_f and S_c that has previously been balanced against the potential difference between X_- and X_+. It will be remembered that in the original potentiometer the voltmeter remained in parallel with the variable points S_c and S_f, while the potential difference between X_- and X_+ was being balanced against that between S_c and S_f, with the aid of a separate zero instrument. With the present arrangement the voltmeter cannot remain shunted across S_c and S_f while it is being used as a detector instrument, and it therefore becomes necessary to examine what is the maximum error that may be introduced hereby.

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* NOTE. It has been pointed out to one of us by Professor C. Drucker, of Leipzig, that the temporary polarisation referred to may be avoided by using horizontal platinum electrodes on which solid quinhydrone is placed.

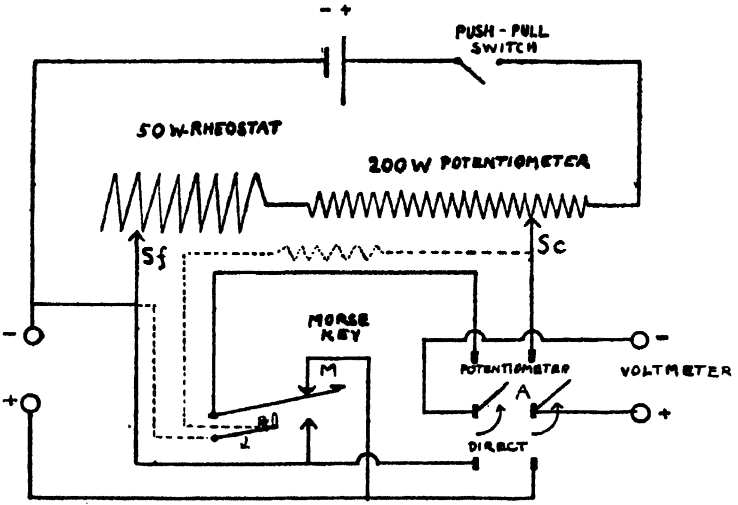
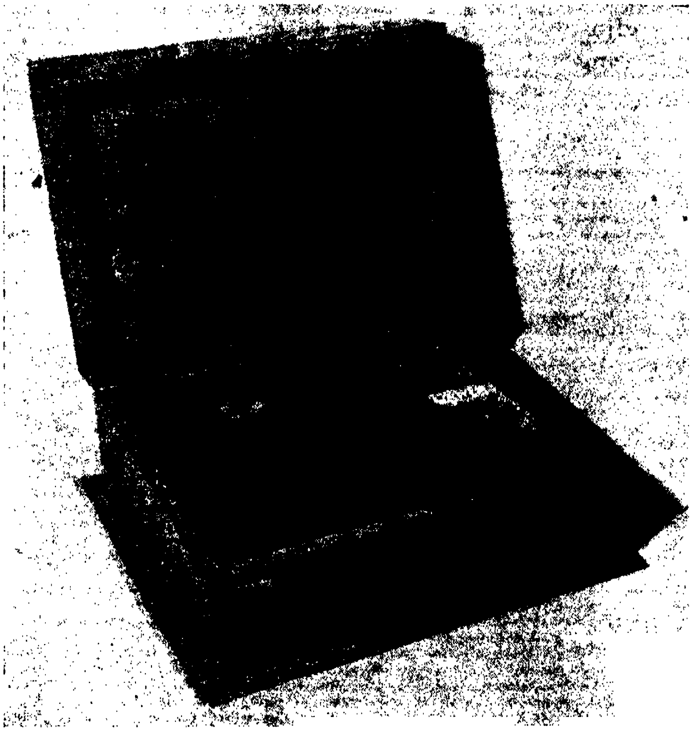


Fig. 2.

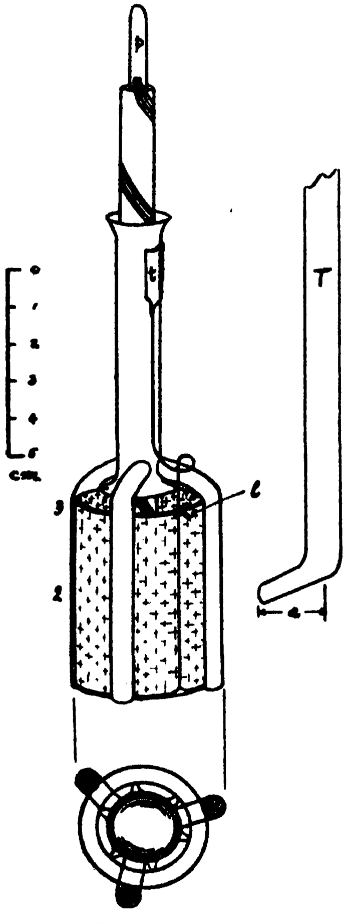
If E be the total E.M.F. of the potentiometer circuit, X the P.D. between S_c and S_f, R the total resistance, and r the resistance between S_c and S_f, then obviously $X = Er/R$.

When the voltmeter is placed in parallel with r, X is altered, since both r and R undergo a slight diminution, which is manifestly the smaller the higher the resistance of the voltmeter. As the calculation of the error is somewhat lengthy, we give only the result. It is found with sufficient accuracy, that the maximum error occurs when $r/R = 2/3$, and is then equal to $(4/27)ER/g = 0{\cdot}15ER/g$, g being the resistance of the voltmeter.

For the dry cell we may take $E = 1{\cdot}5$ volts, for our potentiometer $R = 250$ ohms, and for our voltmeter $g = 50{,}000$ ohms. We thus find that the maximum error occurs at readings of about one volt, and then amounts to 1·1 millivolts. If an error of this magnitude is not permissible it can be reduced by reducing the resistance R of the potentiometer circuit, or it may be eliminated altogether by placing a resistance equal to that of the voltmeter in parallel with r during balancing, and having this automatically switched out when the voltmeter is in use as such. An arrangement of this kind is shown in the dotted portion of the diagram. The potentiometer gives an accuracy which is limited by that of the voltmeter, and for readings of about one volt should, therefore, be the same as that of the Cambridge portable ionisation potentiometer. The absolute accuracy of the readings is uniform throughout, whereas that of the Cambridge potentiometer increases for smaller readings. We have frequently used our potentiometer for p_H measurements and other physico-chemical laboratory exercises.



For purposes of gravimetric electrolytic analysis the potentiometer need only be applied once, after the auxiliary electrode has been selected. The direct-reading voltage v against any arbitrarily chosen working electrode, say copper in copper sulphate solution, and the correct voltage e, are determined. Hence the as well as the gauze, on to the surface of the glass. The stem has an outside diameter of about 8 mm. The construction is usually further simplified by leaving the tube forming the stem completely open, and providing a seating for the lead, which is used as a cement for the silver leading-in peg, *p*, by means of a plug of asbestos wool. The collar formed by the lead must have a wall-thickness of at least 1½ mm., so that there may be sufficient room for its plasticity to come into play, and that cracking may be avoided during changes of temperature. The top of the stem must be rounded-off by fusion. The lead is preferably freed from oxide by melting it, not in its ultimate position, but either in an extension of the stem, which may be cut away later, or in a little funnel made from a tube drawn to a capillary. In either case the oxide is left behind when the lead is run into position.



The quartz-platinum outer electrode has been abandoned and replaced by a platinum cylinder, which is held in position by the separate glass tripod shown. With this arrangement the weight of the platinum need be no greater than in the quartz-platinum electrode. The electrodes we have used weighed between 9 and 10 grms. The method of holding the electrodes has remained essentially the same. The stem of the inner electrode is slipped through the guide tube of the tripod and fitted into its holder or chuck; the outer electrode is pushed inside the tripod, and both it and the tripod are held by the cathode clamp. The leading-in wire, about 0·8 mm. in diameter, is welded to the bottom of the gauze electrode cylinder and attached loosely by a wire loop, *l*, to the top. This construction ensures enough "give" to prevent the wire from breaking on being bent or as a result of vibration. The leading-in wire ends in a tab, *t*, which is held between the tripod and the metal face of the clamp when the electrode is in use. The outer electrode can be taken from the stand without removing the inner one. A cylinder has an advantage over a bell-shaped electrode, since a metal deposit may be removed from it, for further analytical treatment, with a smaller amount of acid. We have found it quite suitable for separations by graded potential, such as that of bismuth or antimony from lead. The tripod is placed in such a position that there may be room for the bend of the auxiliary electrode between two of the legs, the tip of the contact arm being about one cm. below the top of the electrode. The diameter of the outer electrode is 3·2 cm. and its height 5 cm., the diameter of the gauze coating of the inner electrode being about 2·5 cm., and its height about 2·5 cm. In these circumstances the lines of flow of the current should be confined practically to the space between the two electrodes, and the potential difference between the outer electrode and various points in the electrolyte behind and above it should have the same value.

Table I gives the electrode potentials observed when the tip of the auxiliary electrode was at the positions 1 and 3 (see figure), those obtained when it was at 2 being made equal to zero. The solution electrolysed for these experiments was an acid solution of copper sulphate containing 0·25 grm. of copper per 100 ml.

TABLE I

Current in amperes	Electrode potential in millivolts at positions: 1	2	3
0·5	5	0	10
1·0	12	0	7
1·5	15	0	10
2·0	15	0	5
2·5	10	0	20
3·0	10	0	10

It is obviously necessary that the three legs of the glass tripod should have a distance from the axis of the guide tube which is accurately equal to the radius of the electrode cylinder. This can be attained easily in the manufacture of the tripod, when bending the legs into position, by making use of the template, *T*, consisting of a tube or rod which can be pushed into the guide tube, which it fits accurately, the length *a* being equal to the radius of the electrode cylinder.

The method of analysis we have tested is similar to that of Lassieur (*Electro-analyse Rapide*, p. 191), but certain modifications have been found necessary.

The sample (about 0·3 grm.) is dissolved by warming with 10 ml. of concentrated hydrochloric acid, solution being aided, if necessary, by the addition of small quantities of potassium chlorate, and the chlorine being finally boiled off. It is desirable to add 10 ml. of 10 per cent. ammonium chloride solution before the use of chlorate, since, otherwise, tin appears to volatilise as tetrachloride during boiling. When the solution is prepared, 5 ml. of concentrated hydrochloric acid and 1 grm. of hydroxylamine hydrochloride are added, and the solution is diluted to about 100 ml. Electrolysis is commenced with an auxiliary electrode potential of not above 0·40 volt (saturated calomel) at a temperature of 65 to 75° C. At this constant potential the current fluctuations mentioned by Lassieur (*op. cit.*, p. 192) are observed, and a residual current of about 0·3 amp. is attained in about 25 minutes. The auxiliary electrode is flushed out, and the beaker washed down at this stage, after which, electrolysis is allowed to continue for another 5 to 10 minutes. The mixed deposit of copper and antimony is weighed and dissolved in a mixture of 5 ml. of nitric acid (1·42) and 5 ml. of hydrofluoric acid (40 per cent.), and the solution is diluted to 100 ml. The deposition of copper is then carried out precisely as described by Lassieur. Tin may be determined in the liquid from which the copper and antimony have been separated by adding 1 grm. of hydroxylamine hydrochloride and electrolysing at 1 to 1·5 amp. for 15 to 20 minutes. Potential control aids the formation of a good deposit, the saturated calomel electrode being kept at 0·60 volt for most of the time, and, finally, being raised to 0·80 volt.

The following are experimental results obtained by the above method on mixtures of the three pure metals, which were weighed out separately and dissolved together as though they were present in an alloy:

	Taken Grm.	Found Grm.	Taken Grm.	Found Grm.	Taken Grm.	Found Grm.
Copper	0·0135	0·0138	0·0118	0·0128	0·0114	0·0116
Antimony	0·0421	0·0424	0·0488	0·0487	0·0698	0·0698
Tin	0·3045	0·3027	0·3078	0·3063	0·3	—
Copper	0·0122	0·0129	0·0122	0·0126		
Antimony	0·0413	0·0409	0·0413	0·0409		
Tin	0·3	—	0·3	—		

As will be seen, the method is good for the determination of copper and antimony, but is only moderately accurate for tin. Errors of 2 to 3 mgrms. have been obtained with 0·3 grm. of tin. This agrees with the work of Furman (*J. Ind. Eng. Chem.*, 1923, **15**, 1071), who, in criticism of Lassieur's method, states that he always found 1 to 3 mgrms. of tin missing in his analyses (see also Lassieur's defence, *Compt. rend.*, 1924, **179**, 827).

It appears that, in view of the heterogeneous nature of such alloys as these (Lassieur, *op. cit.*, p. 192), the method is sufficiently accurate for most purposes, and has the advantage of rapidity over other gravimetric methods.

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Errata.

The Excretion of Aloes (March issue), p. 154, line 3.—*For* "200 mgrms." *read* "300 mgrms."

The Analysis of Fruit and Fruit Products (April issue).—In the tables on pp. 244–247 the expression

"Mean 1·25SD Mean 2SD"

should read

"Mean *minus* 1·25SD Mean *minus* 2SD"

Notes

The Editor wishes to point out that the pages of the Journal are open for the inclusion of short notes dealing with analytical practice and kindred matters. Such notes are submitted to the Publication Committee in the usual manner.

THE USE OF COMPLEX IONS AS INDICATORS IN ANALYSIS

Indicators for Metals, Etc.

If we consider the equilibrium between a complex ion, such as $Ni(CN)''_4$, and its components in solution, we must have at all concentrations the mass action relation $[Ni(CN)_4'']/[Ni^{\cdot\cdot}] = K[CN']^4$, where K is a constant. This equation is analogous to that for the dissociation of an indicator in alkalimetry, and the complex ion may be used in titrations involving the disappearance of cyanogen ion, instead of hydrogen ion, provided we have a suitable means of estimating either $Ni(CN)_4''$ or $Ni^{\cdot\cdot}$ in solution. Organic reagents for the detection and determination of metallic ions have been largely applied within recent years; where a suitable reagent is available, and certain other conditions are fulfilled, a means can be developed of titrating certain metals in solution.

The method is best illustrated by an example. In principle, any complex (*e.g.* a fluoride or an oxalate) might be used, but only the complex cyanides will be described here. For the purposes of analysis, it is essential that the equilibrium between the complex and its components be set up fairly rapidly, as is the case with such metals as mercury, gold, silver, copper, zinc, cadmium, and nickel. The complexes formed by tervalent iron and cobalt, on the other hand, require too much time for their formation to make them suitable.

A typical reagent, containing the nickel cyanide complex, is made up as follows:—Five per cent. potassium cyanide solution is diluted with an equal volume of alcohol, and excess of solid nickel dimethylglyoxime is added to the solution, which is then boiled and allowed to stand for some time before filtering. The filtrate consists of a saturated solution of nickel cyanide in potassium cyanide, together with free dimethylglyoxime. It is best used at one-tenth the above strength, and will not have the maximum sensitivity unless it has been completely saturated with nickel dimethylglyoxime. If kept over long periods of time, it may require occasional re-filtering.

This reagent may be used in one of two ways:

(A) As a qualitative reagent for those metals, the cyanides of which are less dissociated than that of nickel. In this way the metals, silver, mercury (mercurous and mercuric), cadmium and gold, were found to be detectable when 1 ml. of a 10^{-4} *M* solution was added to 3 ml. of the nickel reagent. Owing to the presence of free dimethylglyoxime in the reagent, nickel also gives a positive reaction, but is distinguished from the above ions by also giving a pink colour with dimethylglyoxime solution. Excess of free acid interferes with the test, but may be neutralised by adding sodium bicarbonate.

The test depends upon the appearance of a pink turbidity, which has a characteristic silky look when viewed against strong diverging light. Ions such as magnesium, beryllium, antimony, bismuth, tin or thallium, which do not form cyanide complexes, give no reaction, but some of the tervalent metals, such as iron and aluminium, form a small amount of gelatinous precipitate at concentrations of about *M*/100, and this is coloured somewhat pink by adsorption of the nickel complex. Bivalent iron attacks the complex only in boiling solution, and zinc, copper and lead interfere with the reagent. The time required for completion of the test increases with dilution, but never exceeds ten minutes.

Test for Formaldehyde.—The reagent was found to be particularly sensitive as a test for formaldehyde. With 3 ml. of a 5.10^{-7} *M* solution added to 1 ml. of reagent a definite silkiness was observed at the end of about one hour, as compared with 3 ml. of distilled water added to 1 ml. of reagent. With acetaldehyde the limit of the test is about 10^{-5} *M* in the same time, and the tests are so faint in comparison with formaldehyde that the reagent can be used to detect it in the presence of acetaldehyde. Schiff's reagent, used under comparable conditions, gave a limit test with formaldehyde in about the same time, at a concentration of 5.10^{-4} *M*.

(B) A few drops of the indicator may be added to standard potassium cyanide solution in a flask, and solutions of salts of silver, mercury or copper run in until a pink colour appears. In principle, all the potassium cyanide is used up before the complex is attacked, but with mercury salts the rate of attack is so slow that it is better to add them to excess of cyanide, and to allow the mixture to stand for some time before back-titrating with silver nitrate. With cadmium salts, the end-point appears to coincide with the formation of the complex $KCd(CN)_3$, but the end-point is not considered as completely satisfactory. Gold salts were not tried, but with *N*/10 silver nitrate solution excellent end-points were obtained, even in artificial light, since the pink nickel compound appears in a fine colloidal form. The last few drops should be added with shaking, and at intervals of not less than thirty seconds. When the titration is complete, a fresh portion of standard cyanide solution may be added to the flask. This re-dissolves the indicator, which may be used in further titrations. The end-point is assumed to coincide with the formation of $KAg(CN)_2$, and is very consistent. In this connection it should be noted that *N*/10 solution of potassium cyanide was observed to lose in strength at the rate of about 0·3 per cent. per day.

USE OF OTHER CYANIDE COMPLEXES.—Attempts were made to use the complex cyanides of cadmium and mercury, in conjunction with diphenylcarbazide, to indicate the liberation of the free ions. Reagents made by dissolving isatin and cuprous cyanide in potassium cyanide solution, and cupric diethyldithiocarbamate in potassium cyanide solution were likewise tried. None of these was as satisfactory as the nickel reagent, partly owing to the fact that the organic indicator used was not sufficiently specific. The extension of the method depends, to some extent, on the discovery of more specific reagents for the metals whose complexes are used, and also on the use of other negative ions besides cyanogen.

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VARIATION IN THE PHOSPHORUS-CONTENT OF MAIZE MEAL USED IN RACHITOGENIC RATIONS

THE Steenbock rachitogenic diet 2965 (Steenbock and Black, *J. Biol. Chem.*, 1925, 64, 274) consists of the following parts:—Yellow maize (meal) 76, wheat gluten 20, calcium carbonate 3, sodium chloride 1. It should give a Ca/P ratio of 4 to 1, and it is essential for the development of corresponding rachitic conditions in rats and for the production of a similar degree of rickets at will that the ratio should not vary much from this value. The object of this note is to draw attention to the possibility of the ratio being variable, owing to considerable fluctuation in the phosphorus-content of yellow maize drawn from commercial sources, and that the ration should not be fed before a chemical analysis of the constituents has been carried out and the calcium carbonate adjusted to suit the Ca/P ratio.

The calcium in 100 grms. of the ration, allowing for an average of 97 per cent. purity of the $CaCO_3$ (on a calcium basis), for 0·016 per cent. of calcium in the maize and 0·140 per cent. in the wheat gluten, is 1·246 grm. The phosphorus-content should then be 0·312 grm. Wheat gluten contains an average of 0·234 (0·193 to 0·275) per cent. of phosphorus, and would account for 0·047 grm., leaving the maize (76 parts) to supply 0·265 grm. The maximum permissible phosphorus-content of the maize is, therefore, 0·265/0·76=0·349 per cent. of air-dry material.

Holmes and Tripp (*Cereal Chem.*, 1933, **10**, 313) have observed a considerable variation in the phosphorus-content of yellow maize grown in the United States, whilst Neal and Becker (*J. Agric. Res.*, 1933, **47**, 249) have found a variation of 0·291 to 0·332 per cent. according to soil conditions. Armsby (*Nutrition of Farm Animals*, New York, Macmillan, 1922, p. 723) gives the average phosphorus-content of maize as 0·303 per cent. (21·5 per cent. of the ash).

During the past few years a considerable number of maize samples from local merchants have been analysed. Widely varying values, mostly higher than the above, have been obtained. The following table illustrates these variations, and gives the Ca/P ratios which would have resulted if such maize had been included in the Steenbock diet.

	Calculated on air-dry maize				
Sample	Moisture Per Cent.	Ash Per Cent.	Phosphorus Per Cent.	$\frac{100\text{P}}{\text{Ash}}$	Ca/P ratio
1	11·16	2·32	0·524	22·6	2·80
2	12·67	1·58	0·382	24·2	3·70
3	12·99	1·52	0·380	25·0	3·71
4	12·48	1·47	0·360	24·5	3·88
5	8·49	1·51	0·355	23·4	3·93
6	12·84	1·52	0·354	23·3	3·94
7	9·99	1·55	0·345	22·3	4·03
8	11·85	1·23	0·278	22·5	4·82
(Armsby	—	1·41	0·303	21·5	4·49)
				Average 23·2	

Six samples of flaked maize gave the following results, respectively:—Moisture, 11·15, 16·60, 15·28, 11·32, 13·95, 13·34; ash, 1·61, 1·60, 1·48, 1·41, 1·42, 1·34; phosphorus, 0·345, 0·341, 0·314, 0·297, 0·297, 0·286 per cent. There was an average of 21·2 (20·9 to 21·4) per cent. of phosphorus in the ash.

Other maize by-products showed a greater variation in ash-content and the phosphorus-content of the ash. The source and type of the maize were, of course, unknown. Seven samples of maize germ meal varied in ash-content from 2·22 to 6·51 per cent., and the phosphorus from 12 to 23 per cent. of the ash. Hominy chop, which contains the bran of the seed, has a higher ash-content than the seed (2·1 per cent.) and phosphorus varying from 19·1 to 23·7 per cent. of the ash. The ash (and the phosphorus) appears to be concentrated in the germ and the bran of the maize seed, and it is obvious that seed containing the greatest proportion of starch to bran plus embryo will have the lowest phosphorus-content. The regularity of the proportion of phosphorus to ash in the seed (average 23·2 per cent.) may be used as an index of the approximate phosphorus-content. It is suggested that the diet may be made up on this approximate basis; the adjustment of the calcium could then be made on the results of analysis of the whole diet.

The table illustrates a range of Ca/P ratio from 2·8 to 4·8 if the recipe for the diet is taken without analysis of the constituents. The importance of analysis, therefore, is obvious, and is further enhanced by possible fluctuations in the moisture-content of maize (most samples, however, contain roughly 12 per cent.) and the possibility of variation in the calcium- and phosphorus-contents of various batches of wheat gluten.

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A NEW METHOD OF APPLYING THE PRECIPITIN TEST

THE method here described is one which, in the opinion of the author, offers certain advantages over the test-tube and capillary-tube methods. It was devised originally for dealing with small quantities of fluids such as the alimentary canal content of mosquitoes and other blood-sucking insects, and it serves this purpose very satisfactorily.

Drops of antiserum are placed on microscope slides and, by means of a glass style, are spread over a small area to form circular films. The films are allowed to dry, and drops of the various test fluids are then deposited on the films. The slides are placed in a moist chamber and examined, after an interval of thirty minutes, under the low power of a microscope.

In a positive reaction the film of antiserum becomes markedly granular, and when disturbed breaks up into insoluble granular fragments, which may in many cases be easily observed with the naked eye. When the reaction is negative the film of antiserum goes into clear solution, and no granular particles are observable microscopically.

A similar method may be used for the approximate estimation of the protein concentration of the fluids under examination. A drop of the fluid is placed on a dry film prepared with a 1 per cent. solution of tannic acid and 1 per cent. acetic acid in physiological saline, and the result is compared with those obtained with serum dilutions of known strength.

The use of drop preparations has proved very serviceable in the testing of insoluble proteins. For example, it was found possible to establish the human origin of a blood stain which had been immersed for three weeks in absolute alcohol; and experimental evidence indicates that in certain protein conjugates, such as protein tannate and picrate, the protein retains its power of being specifically agglutinated when presented as a fine suspension.

Further work on the specific agglutinability of insoluble protein compounds is being carried out, and the results obtained will be reported later.

I have to thank the Director of Medical Services, Uganda, for permission to publish this note.

L. C. HADDON

LABORATORY SERVICES
KAMPALA, UGANDA PROTECTORATE

THE PERKIN TUBE

MR. GARDINER'S note on the Sprengel tube (ANALYST, 1934, 172) reminds me that, while references to the Sprengel tube are fairly frequent, one hardly ever sees mentioned the modification of it devised by Sir W. H. Perkin, and it looks as though this has been forgotten.

Yet the Perkin tube presents great advantages over the Sprengel tube in ease of manipulation; it permits of very accurate work, and it can be readily made, of any size down to very small capacity, by anyone with the very slightest acquaintance with glass-working. The one thing to be careful about is to see that the capacity mark on the one limb is as nearly as possible in the line of the other limb produced backwards. I feel that I am doing chemists a service in drawing their attention to it.

It is figured and described in the *J. Chem Soc.*, 1884, **45**, 443, and an improved form (which is also figured in Thorpe's Dictionary, under "Specific gravity") in the same journal (1896, **69**, 1043).

The apparatus is simply a U-tube, with either end drawn out into a capillary, and these capillaries bent outwards so as to be at right angles to one another. One limb of the U-tube is kept a little shorter than the other, and, in drawing off the capillary at this side, a slight enlargement or bulb is left near its end. The other capillary ends in a narrow point. When the tube is inclined so that this capillary is horizontal, a mark is made on the other capillary (then vertical), at the same level as the horizontal capillary.

The tube is filled by suction, above the mark, and hung in a beaker of water at the desired temperature, until equilibrium of temperature is established. It is then tilted until the exit capillary is horizontal (the shortened limb allows the whole, except the capillaries, to remain under water), and liquid is removed by filter paper until the liquid in the vertical capillary reaches the mark, when the tube is restored to the normal position, and is ready for weighing.

When the tube is righted, the liquid retreats from the point, and no evaporation from the point is to be feared; it rises in the other capillary, and the little bulb provides for any expansion of the liquid, if the temperature of weighing is higher than that at which the density is to be determined.

J. T. Dunn

10, Dean Street
Newcastle upon Tyne

ERASURES AND OFFSETS IN INK WRITING

In the case of *Watts* v. *L.C.C.*, heard in the King's Bench Division, in November, 1932, a legal document was produced bearing an ink mark which might have been made by erasure of a pen stroke or by other means. To determine this point, a microscopic examination with reflected illumination was made, and in conjunction with this, numerous experimental erasures were prepared with a variety of papers, inks and methods of erasure. In each of these experiments the surface of the paper was more or less roughened, and some of the fibres were distorted, partly broken or fibrillated. None of these characteristics was present in the mark under examination, and the distribution of the ink pigment was different in the two cases.

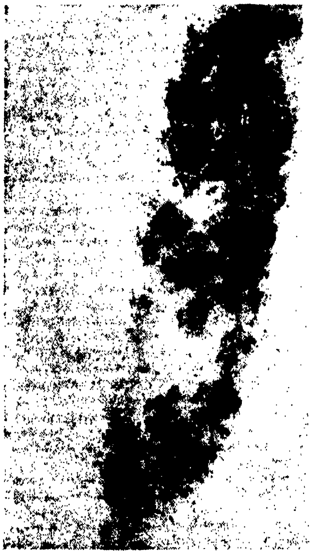

Fig. 1. (Erasure) × 18.

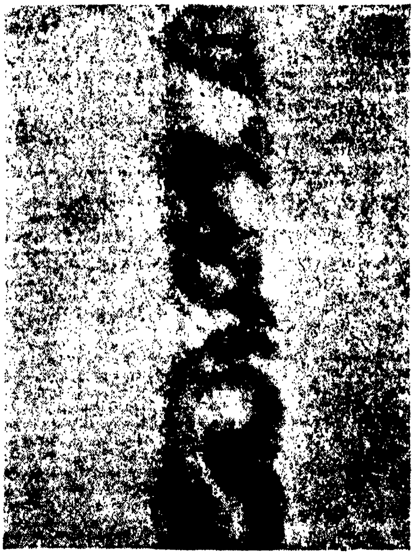

Fig. 2. (Offset) × 18.

These negative results suggested that the mark in question might be an offset from a wet ink stroke on the same or another document, and a number of marks produced in this manner showed considerable resemblance to the one under examination. The accompanying illustrations depict, under a low magnification (× 18), examples of these markings, Fig. 1 showing a partial erasure, and Fig. 2 an offset.

The characteristics of an offset are as follows:—No roughening of the paper surface is apparent, and no loose, broken or frayed fibres are present. The patches of ink pigment forming the mark are usually well defined, with clear-cut edges, often bounded by the paper fibres, and the fibres above the general surface of the paper are evenly pigmented or show a gradual change in intensity along the fibre. The lightly pigmented surface fibres are usually bordered by fine dark lines where the ink has collected in the rounded angle on either side.

Partial erasures, on the other hand, whether made with rubber, ink-eraser or a knife blade, show more or less diffused edges to the patches of pigment remaining, and very irregular pigmentation on the fibres above the paper surface, whilst lightly tinted fibres with dark borders are rarely met with, even on rough-surfaced papers.

T. J. WARD

THE LABORATORY
STAG BREWERY, PIMLICO, S.W.1

Official Appointments

THE Minister of Health has approved the following appointments:

FREDERICK GRANT DUNCAN CHALMERS as Public Analyst for the County Borough of Wolverhampton, in place of A. E. Johnson (deceased) (March 23rd, 1934).

THOMAS REGINALD HODGSON as Public Analyst for the Borough of Hyde, in place of A. E. Johnson (deceased) (March 22nd, 1934).

HENRY TURNER LEA as Public Analyst for the County Borough of Burton-on-Trent, in place of William Partridge (deceased) (March 29th, 1934).

ROY WARREN WATRIDGE as a Public Analyst for the County Council of the Isle of Wight, in addition to S. Ernsley (April 16th, 1934).

HUGH AMPHLETT WILLIAMS as a Public Analyst for the Metropolitan Borough of Deptford, in addition to H. G. Harrison (April 12th, 1934).

Notes from the Reports of Public Analysts

The Editor would be glad to receive the Annual or other Reports of Public Analysts containing matter of special interest to the Society. Notes made from such Reports would be submitted to the Publication Committee.

COUNTY OF KENT

REPORT OF THE COUNTY ANALYST FOR THE FOURTH QUARTER, 1933

THE number of samples of foods and drugs examined under the Food and Drugs Act during the quarter was 978, and the total number during the year was 3655, of which 87 were adulterated. In addition, 3377 samples of milk from individual cows and herds were examined.

MOULD IN BUTTER.—One of the 91 samples submitted during the quarter contained a large number of black spots. These were found to be due to the growth of a mould, the mycelium of the mould running right through the butter.

FISH SOLD UNDER WRONG NAMES.—Four of the 15 fish submitted were found to be untrue to name. The fish purported to be hake, whereas either ling or coalfish had been sold instead.

COMPOSITION OF SHODDIES.—Of the 193 samples of shoddy examined under the Fertilisers and Feeding Stuffs Act, 123 were sold at "unit value," and 12 without a guarantee. Of the 58 samples sold with a warranty, 18 contained too little nitrogen, the deficiencies ranging from 1·3 to 2·32 per cent. With the exception of one sample, which contained 28·8 per cent. of water, the nitrogen deficiencies were not due to excessive water. Many of the shoddies contained considerable quantities of mineral matter, and in almost every instance these shoddies were either fleece combings or wool dust. Five of the samples of fleece combings contained 30 per cent. or more of mineral matter, and the worst sample contained 36·4 per cent. In addition, several of these samples were damp—a condition that has not existed for several years. The results indicate the importance of obtaining a warranty on the purchase of shoddy, or of buying only at "unit value."

Wool Shoddy Manure.—I took exception during the quarter to the sale of some material which was sold as "Wool Shoddy Manure," and which contained only 3·4 per cent. of nitrogen. This manure consisted almost entirely of cotton and vegetable fibre, and I considered, therefore, that it was misdescribed. In my opinion, a wool shoddy should contain at least 50 per cent. of wool, otherwise the term is misleading. The manure could very properly have been sold as a flock dust, and this would not have implied any material proportion of wool. The implied definition contained in the Fertilisers and Feeding Stuffs Act is open to a very wide interpretation, as one definition applies to all manure sold as shoddy, flock dust or wool waste. A shoddy sold as "Best Shoddy" was by no means of high quality, as it only contained 8·6 per cent. of ammonia. The purchaser, however, was given some indication of its manurial value, as it was sold with a warranty of 9·5 per cent. of ammonia.

COMPOSITION OF LIMPETS.—Limpets are to be obtained in considerable quantities on some parts of the coast, and in certain circumstances they are dredged, as they constitute a nuisance. Analyses of wet and dried limpets are as follows:

Water	Nitrogen Per Cent.	Phosphoric acid Per Cent.	Potash Per Cent	Carbonate of lime Per Cent.
70·55	0·40	0·013	—	26·4
4·0	0·54	0·05	0·09	87·1

Dried limpets have, therefore, a distinct manurial value, and form a good source of lime, provided that they are well ground and the shell is finely divided.

F. W. F. ARNAUD

Legal Notes

Under this heading will be published notes on cases in which points of special legal or chemical interest arise. The Editor would be glad to receive particulars of such cases.

METHYLATED SPIRIT IN SAL VOLATILE

A FIRM of druggists was summoned on February 21st at the North London Police Court for having sold sal volatile, in the preparation of which methylated spirit had been used, and for having used the spirit in the preparation of sal volatile.

Mr. Booth, for the Commissioners of Inland Revenue, said that samples of sal volatile purchased from the defendants contained methyl compounds consistent with the article having been prepared with industrial methylated spirits. The offence was regarded as a serious one, having regard to the toxic effects of methylated spirit.

The solicitor for the defence said that there was reason to believe that an assistant of the company was addicted to sal volatile. The defendants had to answer for the default of this employee, who had since been discharged.

A fine of five pounds on each of the three summonses was imposed, with three guineas costs.

Department of Scientific and Industrial Research

WATER POLLUTION RESEARCH

THE ACTION OF WATER ON LEAD, WITH SPECIAL REFERENCE TO THE SUPPLY OF DRINKING WATER*

THIS Report summarises the information collected from the literature on the subject. It is pointed out in the Introduction that the very different, and sometimes contradictory, conclusions that have been drawn from the results of various investigations are accounted for by the great difficulties involved in any attempt to assess the various factors causing the action of water on lead. These factors include the different gaseous and solid constituents of natural waters, the surface condition of the metal, and the varied susceptibility of individuals to lead poisoning.

The Report deals with these factors under the following headings:

Diagnosis of plumbism—Lead-content of drinking water—Protection of consumers against water plumbism—Instances of lead piping in satisfactory use for long periods—Analytical determination of lead—Action of water on lead—Electrolytic action—Allotropy of lead—Over-voltage—Experimental technique and factors influencing results—"Hard" versus "soft" water—Outbreaks of plumbism and protective measures adopted—Aerated mineral waters—Electrical current leakage and lead contamination—Acidity and its correction—Insoluble substances formed in lead pipes—External attack on lead pipes, cables, etc.—Effects on lead of water and dissolved substances—Summary.

The bibliography (13 pages) contains three hundred and seventy-one references, and there is a name index occupying five pages.

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* Technical Paper No. 4. *Summary of Existing Knowledge*, by H. Ingleson, M.A., D.Phil. London: H.M. Stationery Office, pp. 115, 1934. Price 2s. net.

New Zealand

SIXTY-SIXTH ANNUAL REPORT OF THE DOMINION LABORATORY

In his Report for the year 1932 the Dominion Analyst (Mr. W. Donovan, M.Sc., F.I.C.) gives particulars of the chemical analyses and investigations undertaken for the Government Departments. The number of samples examined at the Wellington Laboratory was 5463, and over 2000 samples were analysed at each of the three branch laboratories. Analyses of numerous samples of milk from various parts of the Dominion showed that the quality of the milk is now fairly satisfactory, and in marked contrast with that sold prior to the enforcing of the Sale of Food and Drugs Act.

Identification of Glass Splinters.—A particularly interesting problem, submitted by the Police Department, related to a charge of theft and involved the identification of certain minute splinters of glass. It was shown that the splinters agreed in sp.gr., refractive index, and appearance under ultra-violet light with glass from a broken shop window from which goods had been abstracted, but with no other samples of window or bottle glass that were obtainable.

Manganese Ores and Dry Cell Batteries.—A manganese ore contained 72·0 per cent. of manganese dioxide (= 13·3 per cent. of available oxygen), 0·3 per cent. of manganous oxide, 2·3 per cent. of total iron, with less than 0·02 per cent. of nickel and cobalt, together. The specifications for ore for use in the battery trade usually require at least 80 per cent. of manganese dioxide (=14·72 per cent. of available oxygen), less than 1 per cent. of iron and less than 0·05 per cent. of copper, nickel or cobalt. In addition, physical tests are required; ores with a lower oxygen-content than 14·72 per cent. may be usable if they are sufficiently porous. According to Camp (*Chem. and Metall. Engineering*, March, 1928) the depolarising power of manganese dioxide appears to be not altogether dependent on its MnO_2 content. In different lots of the same type, however, the depolarising quality is directly proportional to the MnO_2 content. Also, Camp regards a proportion of ferric oxide up to 3 or 4 per cent. as harmless, but the presence of metallic iron is very deleterious.

Another manganese ore, from Whangarei, contained 89·6 per cent. of manganese dioxide (= 16·5 per cent. of available oxygen), with less than 0·01 per cent. of copper, 1·0 per cent. of total iron, and less than 0·02 per cent. of nickel and cobalt. This was reported as of good quality for chemical use.

Diatomaceous Earth as Filtering Medium.—Two samples from Matamata County gave the following results:—Silica, 83·40, 80·55; loss on ignition, 12·06, 12·42; and residue (chiefly oxides of iron and alumina), by difference, 4·54, 7·03 per cent. Both samples consisted largely of *Melosira*, a small cylindrical form which is the chief form found in many New Zealand diatomites. Associated with it were fairly numerous larger and needle-shaped species, the following being identified: *Cocconema lanceolatum*, *Pinnularia* (very large forms), *Navicula cuspidata*, *Tabellaria* and *Epithemia turgida*. In No. 1 there were present also numerous sponge spicules. No. 2 contained diatoms like those in No. 1, but with a larger proportion of very fine species—*viz*. Diatoma.

With regard to the suitability of the samples for filtration purposes, it is generally considered that the best material is a mixture of diatoms of various shapes, in which those of a thin needle-shaped form predominate. A deposit of diatomaceous earth obtained from California, and said to consist chiefly of a mixture of thin disc-shaped forms (*Coscinodiscus*) and rod-like forms (*Synedra*), together with sponge spicules, is claimed by the owners (The Celite Co., U.S.A.) to be very efficient as a filtering medium. Diatomites, consisting chiefly of the small cylindrical diatom *Melosira*, are not usually considered suitable for filtration purposes.

Another sample (Rotorua County) was composed chiefly of the diatom *Melosira*, varying little in size. An appreciable quantity of transparent fragmentary glass was also present. The sample could not be recommended as particularly suitable for filtration purposes. Diatomite is used to a considerable extent in the United States and elsewhere as an ingredient in Portland cement concrete to improve workability and resistance to disintegration, especially for marine work. The other major use is for heat, cold, and sound insulation. The sample might find some application in New Zealand along such lines. The presence of the fragments of volcanic glass would detract somewhat from its value as an insulator, but would tend to enhance its value for concrete-making.

Tests on Anaesthetic Chloroform.—A sample complied with the tests given in the British Pharmacopoeia, 1914, and United States Pharmacopoeia, and also with the more rigid tests recommended by Baskerville and Hamor (*J. Ind. Eng. Chem.*, 1912, 4).

The resorcinol-vanillin test of Allport (Analyst, 1931, **56**, 706) gave a slight positive result for hydrochloric acid, indicating incipient decomposition. Allport's test for hydrochloric acid was found to be much more delicate than the silver nitrate test (British and United States Pharmacopoeias), the barium hydroxide test of Baskerville and Hamor, or the benzidine test of the German Pharmacopoeia.

Food Preservatives in Germany*

The Draft Regulations, published in 1932, are expected shortly to become statutory. Only certain specified substances are permissible as preservatives, and these must comply with the standards of the German Pharmacopoeia. The sale of mixtures of preservatives other than those mixtures appearing in the official list is prohibited, as is also the sale of preservatives mixed with other substances, with the exception of mixtures containing salt, sugar, tartaric acid, citric acid, and mixtures of the ethyl and propyl esters of *p*-hydroxybenzoic acid with sodium carbonate.

Preserved foodstuffs sold in packages must be labelled "chemically preserved," or "chemically preserved with boric acid" when boric acid is present.

The approved preservatives comprise the following, to be used in the amounts specified per 100 grms. of foodstuffs:

Ethyl and Propyl Esters of p-*Hydroxybenzoic Acid including their Sodium Compounds and their Mixtures.*—Fish and crustacean products, 50 mgrms.; salmon, 25 mgrms.; salmon substitute, 25 mgrms.; preserved eggs: liquid egg yolk, 800 mgrms.; margarine, 80 mgrms.; preserved vegetables, pickling liquors, 80 mgrms.; fruit preparations (other than cherry, orange and lemon juices), 90 mgrms.; cherry juice, orange juice, lemon juice, 90 mgrms.; fruit pulp and fruit butters, 90 mgrms.; liquid fruit pectin, 90 mgrms.; non-alcoholic drinks, 50 mgrms.; confectionery, chocolates, 120 mgrms.; ices, 15 mgrms.; coffee extracts and substitutes, 100 mgrms.; malt extract with water-content of 20 to 25 per cent., and in packages of 5 kilos. and over, 50 mgrms.

Hexamethylene-tetramine.—Fish and crustacean products, 25 mgrms., in addition to the above esters (50 mgrms.); fish roes, German roe, caviare, 100 mgrms.; crabs' claws, etc., 50 mgrms.

Hydrogen Peroxide.—Fish in jelly ("Bratmarinaden"), 200 mgrms. in the jelly in addition to the esters (50 mgrms.).

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* *Food Manufacture*, 1934, **9**, 102.

Benzoic Acid.—Salmon substitute, 500 mgrms.; crabs' claws, etc., 500 mgrms. (alternative to hexamethylene-tetramine); caviare, 500 mgrms. (alternative to hexamethylene-tetramine); crabs, tinned crabs, 900 mgrms.; preserved eggs: liquid egg yolk, 1000 mgrms., or 1200 mgrms. of sodium benzoate (alternative to the esters; *supra*); margarine, 200 mgrms., or 240 mgrms. of sodium benzoate (alternative to the esters, *supra*); preserved vegetables, pickling liquors, 200 mgrms., or 240 mgrms. of sodium benzoate (alternative to the esters, *supra*); fruit preparations and juices (other than cherry, orange and lemon juice), 180 mgrms. of sodium benzoate (or formic acid, sulphurous acid, potassium sulphite or esters); cherry juice, orange juice, lemon juice, 180 mgrms. of sodium benzoate (or formic acid, sulphurous acid, potassium sulphite or esters); fruit pulp and fruit butters, 150 mgrms. (or 180 mgrms. of sodium benzoate (as alternative); liquid fruit pectin, 180 mgrms. of sodium benzoate; non-alcoholic drinks, 50 mgrms. of sodium benzoate (as alternative); chocolate and confectionery, 150 mgrms. (alternative to esters, *supra*); ices, 100 mgrms. (alternative to esters, *supra*); edible mustard, 150 mgrms.

Boric Acid.—Anchovies, 500 mgrms.; caviare, 500 mgrms. (alternative to hexamethylene-tetramine); crabs: tinned crabs, 900 mgrms.; liquid egg yolk intended exclusively for use in fancy bakeries but not in the production of dietetic foods, 1500 mgrms.

Formic Acid (25 *per cent. Solution*).—Fruit preparations and fruit juices other than cherry, orange and lemon juices, 1000 mgrms. (alternative); cherry, orange and lemon juices, 1600 mgrms. (alternative); liquid fruit pectin, 1000 mgrms. (alternative).

Sulphurous Acid.—Horseradish preparations, 75 mgrms. (as SO_2), or 125 mgrms. of sodium bisulphite; fruit preparations and juices; also cherry, orange and lemon juices, 125 mgrms.; or 435 mgrms. of potassium "pyrosulphite" (alternatives); fruit pulp and fruit butter, 125 mgrms. or 435 mgrms. of potassium "pyrosulphite" (alternatives); fruit juice used directly as a beverage, excepting grape juice, 12·5 mgrms.; dried fruit, 200 mgrms.; edible gelatin, 125 mgrms.

In the preparations of jams, marmalades, etc., benzoic acid, sodium benzoate, formic acid or the esters mentioned above may be used in aqueous or alcoholic solution for wetting parchment paper used as covering for the product packed for sale.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs Analysis

Acid-content of Tomato Purée. G. Mészáros. (*Z. Unters. Lebensm.*, 1934, 67, 319–321.)—Different brands of tomato purée vary appreciably as regards their acid flavour, the acidity being due, not only to the organic acids occurring in the raw tomatoes, but also to lactic fermentation of the carbohydrates present. To determine the acidity, 50 to 60 grms. of the purée from the middle of the container are thoroughly mixed, and 1 to 2 grms. are weighed out. This is shaken with 70 to 80 ml. of water for 6 to 8 minutes, and the whole is then made up in a measuring flask to 100 ml. and again well shaken. About 15 ml. are then centrifuged, and 10 ml. of the liquid are afterwards titrated with 0·25 *N* sodium hydroxide solution in presence of phenolphthalein. The result is expressed as ml. of *N* sodium hydroxide per 100 grms. of purée. For six different brands containing, respectively, 25·6, 26·9, 20·5, 20·3, 7·5, and 9·1 per cent. of dry matter, the acidities found were 30·2, 29·7, 24·6, 18·8, 15·5, and 37·8. The contents of different containers of one and the same brand showed somewhat varying acidities. Determinations of the lactic acid yielded discordant results, although they indicated that the acidity of tomato purée is due mainly to this acid. T. H. P.

Keeping Quality of Frozen Orange Juice. M. A. Joslin and G. L. Marsh. (*Ind. Eng. Chem.*, 1934, **26**, 295–299.)—Frozen orange juice stored at −18° C. deteriorates in flavour when oxygen is present. If the juice is deaerated previously and stored in an atmosphere of nitrogen, it retains its flavour for months. Flash pasteurisation at about 80° C., with rapid cooling previous to freezing and storage, is also a means of retaining the flavour. W. P. S.

Transition Points of Mixtures of Cow's Butter and Cocoa Butter. D. W. Horn and M. A. Wilson. (*Amer. J. Pharm.*, 1934, **106**, 59–61.)—The transition point of a mixture of fats is found by placing the melted fat in a Dewar test-tube held in the centre of a bath of water and ice. The fat is stirred constantly with a glass stirrer encircling the thermometer inserted in the fat. The temperature is recorded every minute from the time it has dropped to 30° C., and the results are plotted, temperatures vertically and times horizontally; they invariably yield a graph suggestive of the sign $\surd$. Sub-cooling to as much as 5 or 10 degrees may occur before crystallisation sets in accompanied by a gradual rise in temperature. The rise stops at a definite temperature which is held for several minutes, and is called the transition point. A study of mixtures of cow's butter and cocoa butter gave the following observed transition points (agreeing almost exactly with the theoretical values). Percentage of cow's butter 0, transition point, 29·2° C.; 20 per cent., 26·2° C.; 40 per cent., 22·6° C.; 60 per cent., 19·4° C.; 70 per cent., 17·6° C. Up to 70 per cent. of cow's butter there is a linear relation expressed as $y = -0{\cdot}165x + 29{\cdot}2$. The transition point is regarded as useful in factory control, although it is not a substitute for the Reichert–Meissl value.

D. G. H.

Adulteration of Cocoa Butter. Determination of the "Azelaic Acid" Values of Palm and Illipé Butters. G. Schuster. (*J. Pharm. Chim.*, 1934, **126**, 206–209.)—The procedure previously described (ANALYST, 1933, **58**, 763) may be simplified as follows:—After oxidation, the insoluble brown mass (potassium salts of azelaic glycerides mixed with manganese dioxide) filtered off is dried in a vacuum over sulphuric acid to expel all traces of acetone. The powder thus obtained is extracted for about 30 minutes in a Soxhlet apparatus with boiling alcohol (7 to 8 times the weight of the original fat). The potassium salts of the azelaic glycerides and the pelargonate dissolve in the alcohol, a small amount of which is oxidised to acetaldehyde by the excess of permanganate remaining in the dried mass. The hot alcoholic solution is treated with excess of concentrated magnesium chloride solution at the same temperature. The subsequent operations are as already described (*loc. cit.*). The mean azelaic acid value was 121·1 for illipé butter, and 132·8 for palm butter. T. H. P.

Gadoleic Acid in Cod-liver Oil. Y. Toyama and T. Tsuchiya. (*J. Soc. Chem. Ind. Japan*, 1934, **37**, 14–17B.)—The methyl esters (3000 grms.), resulting from the action of methanol on the oil at room temperature in the presence of potassium hydroxide, were fractionated, and the lithium salts of the fatty acids, liberated from the fraction of b.pt. 210° to 225° C. at 10 mm. pressure (yield 594 grms.) were extracted with 50 per cent. alcohol. The insoluble portion (mainly salts of mono-ethylenic acids with some derived from saturated acids) was acidified with hydrochloric acid, the acids being distilled as methyl esters, and the fraction (59 grms.) of b.pt. 217° to 221° C. at 10 mm. pressure was treated by the lead salt and alcohol method with a quantity of lead acetate equivalent to about 10 per cent. of the fatty acids. The unsaturated acids in solution were recovered by evaporation and purified by repeated re-crystallisation from 80 per cent. alcohol, when gadoleic acid was obtained in needles, having sp.gr. at 25°/4° C., 0·8882; n_D^{25}, 1·4597; m.pt., 24° to 24·5° C.; neutralisation value, 179·9; and iodine value, 81·0. On hydrogenation they yielded arachidic acid, the identity of which was established by the mixed melting-point method. The colourless syrupy ozonide remaining after passing ozonised oxygen through a solution of 4 grms. of the acid in 40 ml. of chloroform and evaporating, was decomposed in 40 ml. of boiling water, and the cool solution was extracted with 400 ml. of ether, which were evaporated. The new residue was then extracted 3 times with 40 ml. of hot petroleum spirit, the solid which separated on cooling being added to the other insoluble matter (total 1·3 grm.). (*a*) The solution obtained at this stage yielded 1·7 grms. of colourless distillate when distilled under 100 mm. pressure at temperatures up to 215° C., and this was mixed with a slight excess of potassium carbonate solution and shaken with ether in order to separate the neutral matter, the acidic portion being liberated from the soap solution and re-crystallised from 60 per cent. alcohol (neutralisation value, 300·1; m.pt., 27° C.). This was identified with undecanoic acid by the mixed m.pt. method, in which the acid prepared by hydrogenation of undecenoic acid obtained by dry distillation of castor oil was used. The neutral substance in the ether gave Schiff's reaction for aldehydes. The residue from distillation was treated with an alkaline solution of potassium permanganate, and the residue left after evaporation of an extract of the oxidation products in ether was extracted with hot water. A crystalline solid (neutralisation value, 592·0; m.pt., 102° to 103° C.) was deposited from the cool solution, and was probably impure azelaic acid. (*b*) An extract in hot water of the white residue insoluble in petroleum spirit was oxidised with potassium permanganate, and the liquid was extracted with ether. This removed a substance which was shown (by the mixed melting-point method) to be azelaic acid. It was then deduced that the constitution of gadoleic acid is

$$CH_3(CH_2)_9\,CH{:}CH(CH_2)_7.\ COOH,$$

namely, the same as that given by Takano (*id.*, 1933, **36**, 131) for the eicosenoic acid from Japanese sardine oil, and the identity of the two acids is therefore established (see also, Toyama, *id.*, 1925, **28**, 95; 1926, **29**, 531, 538; 1927, **30**, 63, 116, 207, 519; ANALYST, 1927, **52**, 245; Tsujimoto, *id.*, 1926, **51**, 49; Hilditch and Lovern, *id.*, 1928, **53**, 352; and also following abstract).

J. G.

Identification of Gadoleic Acid in Japanese Sardine Oil, Herring Oil and Liver Oil of "Sukeso-Dara" (*Theragra Chalcogramma*). Y. Toyama and T. Tsuchiya. (*J. Soc. Chem. Ind. Japan*, 1934, **37**, 17–20B.)—The methods used were essentially the same in principle as those described in the preceding abstract, exceptions being indicated below. In the case of Japanese sardine oil the fraction (b.pt. above 215° C., at 10 mm. pressure) of the ethyl esters obtained by ethanolysis of the oil, was treated by the sodium salt and acetone method, the fatty acids liberated from the insoluble sodium salts being converted into the methyl esters which, when distilled, gave a fraction of b.pt. 218 to 225° C. (at 10 mm.). The lithium salts of the acids of this fraction which were insoluble in 50 per cent. alcohol were then separated and decomposed by acid, and were treated by the lead salt and alcohol method, as before (*loc. cit.*), the unsaturated acids being again converted into the methyl esters. The fatty acids from the fractionation of these (b.pt. 217° to 221° C., at 10 mm.) were again purified by the lithium salt process to remove the last traces of highly-unsaturated acids, and pure gadoleic acid was finally obtained by repeated re-crystallisation, from 80 per cent. alcohol of the acids from the insoluble lithium salts. Hydrogenation of the gadoleic acid gave arachidic acid; oxidation by Hazura's method gave a dihydroxy-arachidic acid in lustrous leaflets, m.pt. 128° to 128·5° C.; and the elaidin reaction gave a product of m.pt. 51·5° to 52° C. Ozonisation was then applied, as described before (*loc. cit.*), and the production of undecanoic and azelaic acids confirmed the structure of gadoleic acid already deduced. Herring oil and the liver oil of "sukeso-dara" were investigated in a similar way, and with the same final result. In the latter case the acid was not examined by ozonisation, although its identity was confirmed by the mixed melting-point obtained with gadoleic acid from cod-liver oil. The values of the original liver oil were:—sp.gr. at 15°/4° C., 0·9231; n_D^{15} 1·4798; acid value, 2·4; saponification value, 183·3; iodine value, 150·1; unsaponifiable matter, 0·92 per cent. J. G.

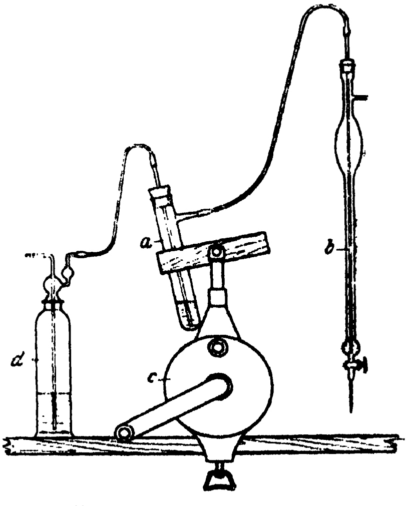
Fatty Substances of Shell-Fish. M. Tsujimoto and H. Koyanagi. (*J. Soc. Chem. Ind. Japan*, 1934, **37**, 81B.)—I. *Shell-Fish in the Group Pelecypoda.*—The fatty matter amounts to about 0·7 per cent. of the undried fish (free from shell). Of this amount, more than half consists of phosphatides, the fatty acids of which have high iodine values. Unsaponifiable matter may reach 45 per cent. It contains a peculiar sterol which forms an acetate of high m.pt., and shows a characteristic red colour reaction in acetic anhydride solution when a drop of strong sulphuric acid is applied. The author considers that this sterol may be identical with clionasterol (Dorée, *Biochem. J.*, 1909, 92).

II. *Shell-Fish in the Group Gasteropoda.*—The fatty matter amounted to 1 per cent., and the phosphatides to about 40 per cent. for ear-shell (*Haliotis gigantea*), and about 61 per cent. for top shell (*Turbo cornutus*). The unsaponifiable matter was about 20 per cent. and 38 per cent., respectively. It consisted chiefly of cholesterol, but also contained some of the more uncommon sterol found in the *Pelecypoda*. R. F. I.

Constituents of Menuke Oil. S. Ueno and M. Iwai. (*J. Soc. Chem. Ind. Japan*, 1934, **37**, 52B.)—The menuke fish, which belongs to the family

Scorpaenidae, is found in the Sea of Japan. The oil is orange-yellow, and has an odour similar to that of herring or shark oil. The specimen examined had the following constants:—Sp.gr. at 20/4° C., 0·9155; n_D^{20}, 1·4721; acid value, 2·83; saponification value, 181·8; iodine value, 107·2; Reichert–Meissl value, 0·51; unsaponifiable matter, 1·40 per cent. By the lead salt and ether process 12 per cent. of solid fatty acids and 88 per cent. of liquid fatty acids were found. The solid fatty acids contained 70 per cent. of palmitic acid and relatively small amounts of stearic and myristic acids. The liquid fatty acids belonged chiefly to the oleic acid series, and contained oleic (chiefly), with smaller amounts of the acids $C_{16}H_{30}O_2$, $C_{20}H_{38}O_2$ and $C_{22}H_{42}O_2$. In the more unsaturated series clupanodonic acid was the chief constituent. R. F. I.

Auto-oxidative Rancidity of Fats. VI. Technique and Evaluation of the Kreis Reaction. K. Täufel and P. Sadler. (*Z. Unters. Lebensm.*, 1934, **67**, 268–273.)—The Kreis reaction of fats depends on the formation of epihydrinaldehyde owing to auto-oxidation of the fatty material. Fats may undergo degradation in other ways, and in such cases the Kreis reaction fails. As auto-oxidation proceeds, the proportion of epihydrinaldehyde increases to a certain point, but, finally, it may become constant or even diminish. Strict parallelism between the intensity of the Kreis reaction and the extent to which auto-oxidation has proceeded cannot, therefore, be expected. This reaction is usually carried out by shaking the oil or melted fat with concentrated hydrochloric acid and adding a solution of phloroglucinol in ether. Such procedure renders the reaction liable to disturbance from various causes. For instance, red colours are yielded by a number of substances, including allyl alcohol, allylamine, diallylcarbamide, eugenol, etc. Moreover, if the aldehyde concentration has greatly increased owing to advanced deterioration of the fat, sparingly soluble, colourless aldehyde phloroglucides are formed, the Kreis colour reaction being prevented. Difficulty may also arise if the product being tested has appreciable colour. Interference from any of these causes is avoided by either of the two following alternative procedures.



(i) *Cotton-wool Plug Method.*—The oil or carefully-melted fat is mixed in a short test-tube with an equal quantity of concentrated hydrochloric acid (ice-cooled). A cotton-wool plug, inserted in the tube at its upper dry part, is moistened with about 1 ml. of 0·1 per cent. solution of phloroglucinol in alcohol and 10 drops of hydrochloric acid (at least 20 per cent.). The tube is well shaken for 1 to 2 minutes without splashing the cotton, and may, if necessary, be gently heated (to about 40° C.). Red coloration of the lower surface of the plug indicates epihydrinaldehyde. (ii) *Crucible Method.*—The test-tube is replaced by a tall porcelain crucible covered with filter-paper kept moistened with the reagent.

To obtain an approximately quantitative measure of the epihydrinaldehyde, use is made of the apparatus shown in the figure. From 2 to 3 ml. of the oil, and the same volume of concentrated hydrochloric acid, both ice-cold, are placed in *a*, which is immersed in ice-water, and is connected with a gas-washing bottle, *d*, and an absorption tube, *b*, containing, in its lower bulb, an ice-cooled mixture (1: 1) of the alcoholic 0·1 per cent. phloroglucinol solution and concentrated hydrochloric acid. A stream of air, sufficiently rapid to force the reagent into the upper bulb of the absorption tube, is drawn through the apparatus. Liberation of the epihydrinaldehyde may be accelerated by shaking the tube *a*, and is then usually complete in 30 minutes. If a phloroglucide precipitate appears in *b*, the test must be repeated with a smaller quantity of the oil. When a solid fat is to be tested, gentle warming of *a* becomes necessary, but the temperature should be kept as low as possible. The contents of the absorption tube are compared in a colorimeter with standard tubes prepared with known amounts of epihydrinaldehyde. This procedure does not affect glycerides, but, when it is applied to free linolic acid, epihydrinaldehyde is gradually formed, owing to oxidation of the acid by the oxygen of the air-current. Danger of such oxidation is avoided by replacing the stream of air by one of nitrogen or carbon dioxide. (*Cf.* Täufel, ANALYST, 1931, **56**, 541.)

T. H. P.

Photochemical Studies of Rancidity. N. R. Coe and J. A. Le Clerc. (*Ind. Eng. Chem.*, 1934, **26**, 245–248.)—Colour tests for rancidity and the peroxide test for the decomposition of an oil may not indicate conclusively that an oil is rancid, and these tests are not reliable when applied to oils which have been protected from light. Oils protected from light by opaque black paper, or by green paper transmitting light delimited by 490$m\mu$ to 580$m\mu$, remain free from rancidity even after seven months, although they give strong positive tests with both the Kreis and the von Fellenberg reagents, and have peroxide values equal to, or higher than, that of an unprotected oil which has become rancid. Similar results are obtained when air has been bubbled through the oils at the rate of 6 litres per hour. Oxidation rancidity appears to be due to photochemical action on a compound which probably exists simultaneously in the oil, or is produced from compounds which give rise to the formation of peroxides.

W. P. S.

Photochemistry of Cod-liver Oil. J. H. Graham. (*Amer. J. Pharm.*, 1934, **106**, 44–56.)—It has been found that the golden-yellow fluorescence of cod-liver oil exposed to light of sufficient intensity disappears in about 90 days, leaving a pale yellow or almost colourless oil. At the same time, the pink colour of the Kreis test, given at first with all the four oils used, develops more quickly with the lapse of time, giving rise to a faint purple, or, with specimens kept in the dark, to a deep red colour. However, the Hagar–Salkowski reaction is regarded as more conclusive in determining the effects of light exposure and rancidity (that is, the relative freshness of the oil), than the apparently more delicate Kreis test. In the former test a violet or purple colour, changing slowly to brown on the addition of one drop of concentrated sulphuric acid to a solution of one drop of oil in one ml. of chloroform, indicates possible freedom from rancidity.

In the oils kept for 90 days the formation of the purple colour was gradually replaced by the immediate development of the brown colour, followed by a brown precipitate. No consistent correlation was found between saponification, iodine, and free acid values, and variations of air, moisture, light and temperature conditions seem to preclude it. The chemical complexity of cod-liver oil is emphasised; important chemical changes take place rapidly if proper conditions are not maintained, such as exclusion of excessive moisture, light and air, and the maintenance of comparatively low and uniform temperatures. D. G. H.

Analytical Constants of Peanut Butter. **H. L. Wikoff, M. Busey and A. M. Kaplan.** (*Ind. Eng. Chem.*, 1934, **26**, 291–292.)—Peanut butter consists of the finely-ground whole nuts. Ten different brands contained from 0·8 to 3·7 per cent. of moisture, and the dry samples yielded:—Ash, 1·91 to 3·18; acid-insoluble ash, 0·07 to 0·25; oil, 39·45 to 52·34 per cent. The dry, oil-free meals contained:—Proteins, 54·64 to 62·45; sodium chloride, 1·08 to 3·45; total reducing substances, expressed as dextrose, 22·77 to 29·92; crude fibre, 2·67 to 4·31; starch, 14·46 to 21·43; pentosans, 5·30 to 6·81 per cent. The variation in the amount of chloride is due to the fact that common salt is added as a seasoning agent.

W. P. S.

Assay of Strychnine Alkaloid in Strychnine Sulphate Tablets. **F. J. Amrhein.** (*Amer. J. Pharm.*, 1934, **106**, 57–58.)—The official method of the A.O.A.C. for the determination of strychnine in tablets takes no account of the presence of interfering fillers or of mineral oil added as a lubricant in the manufacture. To overcome error due to these sources, the following modified method is advocated:—The tablets (25 to 100) are weighed and placed in a separating funnel, and 20 ml. of water and 1·2 ml. of 10 per cent. sulphuric acid are added. After complete disintegration, two extractions are made with 25-ml. portions of chloroform; the liquid is then made alkaline with ammonia water (1+2), and five extractions are made with 25, 20, 15, 10, and 5 ml., respectively, of chloroform, or until the alkaloid is completely removed. The first two extracts are placed in a separating funnel plugged in the stem with absorbent cotton wet with chloroform, and washed with 5 ml. of water containing a drop of the dilute ammonia. The clear chloroform layer is removed, and each successive chloroform extract is washed with the same wash water and filtered, the outside of the funnel stem being also finally washed with chloroform, which is added to the main portion. The combined extracts are evaporated on a steam bath, but the drying of the final 3 to 5 ml. is finished in a current of air. Two to 3 ml. of neutral alcohol are added, the mixture is warmed, and the solution is titrated with 0·02 N acid (methyl-red as indicator) until a faint pink tint appears, when 50 ml. of boiled water are added, and the titration is continued to a faint red end-point. One ml. of 0·02 N acid is equivalent to 6·684 mgrm. of strychnine. With 1/40 grain tablets the method gave 1/40 grain of strychnine, and, with 1/60 grain tablets, 1/60 grain, whereas the regular A.O.A.C. method gave results for 1/40 grain tablets varying from 1/48 to 1/50 grain, and 1/60 grain tablets were returned as 1/90 grain.

D. G. H.

[Hydrocyanic Acid in] Tobacco Smoke. IV. E. Waser and M. Stähli. (*Z. Unters. Lebensm.*, 1934, 67, 280–284.)—The method used for determining the content of hydrocyanic acid in cigarette smoke was a modification of that used by Lehmann and Gundermann (*Arch. Hyg.*, 1912, 76, 98) for cigar smoke. The smoke was washed with dilute sulphuric acid to remove tarry constituents, filtered through cotton wool, and passed into a definite volume of standard silver nitrate solution containing nitric acid, distributed between three absorption flasks. The silver cyanide (always found free from thiocyanate) thus formed was converted, by addition of ammonia solution, into silver ammonium cyanide. The solution thus obtained is clear and colourless, so that purification with animal charcoal, which might result in some adsorption of the double cyanide, is unnecessary. By dropwise addition of concentrated nitric acid, silver cyanide was precipitated and, after removal of this by filtration, the residual silver in the solution was determined by titration with standard ammonium thiocyanate solution. The proportion of hydrogen cyanide in the smoke from cigarettes of various kinds was found to vary between 0·020 and 0·034 per cent. of the dry matter of the tobacco smoked. The amount found is independent of the nicotine-content of the tobacco and, for any one type of cigarette, is constant under constant conditions of smoking, although it increases with the rapidity of smoking. The amounts of hydrogen cyanide found are considered too small to constitute any direct danger to the smoker.

T. H. P.

Determination of Arsenic in Medicinal Organic Compounds. E. Kahane. (*J. Pharm. Chim.*, 1934, 19, 116–123.)—*Destruction of Organic Matter.*—To a sample of the compound weighting 0·2 to 0·4 grm. are added 5 ml. of an acid mixture containing 700 ml. of concentrated sulphuric acid, 100 ml. of concentrated nitric acid and 200 ml. of perchloric acid (sp.gr. 1·61), and the whole is heated until fumes of sulphuric acid are given off; the addition of a few drops of a mixture of 2 vols. of perchloric acid and 1 vol. of nitric acid, and further heating, may be necessary to produce a colourless liquid. The arsenic in the solution is present in the quinquevalent form. *Determination of Arsenic.*—Whilst many of the usual methods are applicable, the following modification of the bromate process is preferred:—To the colourless sulphuric acid liquid, about 0·25 grm. of hydrazine sulphate crystals is added, and the liquid is heated for 10 minutes in order to reduce the arsenic to the tervalent form, and to decompose the excess of the reducing agent. The solution is cooled before and after the addition of 20 ml. of water, 0·1 to 0·2 grm. of potassium bromide is added, and the solution is titrated with standard potassium bromate solution until a faint yellow colour (due to free bromine) appears; this is stated to afford a more sensitive indication of the end-point than the more usual expedient involving the bleaching action of the free bromine on an added dye, *e.g.* methyl orange; 1 ml. of 0·1 *N* potassium bromate solution ≡ 3·75 mgrms. of arsenic. Good results were obtained with a wide range of organic arsenic compounds.

S. G. C.

Biochemical

Heavy Water Content of the Water in Milk. H. Erlenmeyer and H. Gärbner. (*Helv. Chim. Acta*, 1934, **17**, 334.)—The authors have previously described (*Helv. Chim. Acta*, 1934, **17**, 30) an apparatus with lead electrodes, by means of which the electrolytic decomposition of 8 litres of ordinary pure water yielded 20 ml. of heavy water of sp.gr. 1·00087. In view of biological differences in the effects of ordinary water and heavy water, the experiment was repeated on 8 litres of the water obtained from milk of undoubted purity. This also yielded 20 ml. of heavy water of sp.gr. 1·000832, and the conclusion is, therefore, drawn that the water of milk has the same composition as ordinary water, and that the biological filtration of the water in the process of the formation of milk does not lead to an increase in the proportion of the toxic heavy water.

Colorimetric Method for Determination of Glucosamine and Chondrosamine. L. A. Elson and W. T. J. Morgan. (*Biochem. J.*, 1933, **27**, 1824–1828.)—These substances are heated in alkaline solution with acetylacetone, and thus converted into pyrrole derivatives, which, on treatment with Ehrlich's reagent (*p*-dimethylaminobenzaldehyde in acid solution) in the presence of alcohol, give rise to very stable red solutions. Results show that the error of determination is less than 5 per cent. if the amount of glucosamine hydrochloride is within the range 0·75 to 3·0 mgrm., and if the colour intensity of the standard glucosamine hydrochloride solution does not differ by more than 25 per cent. from that of the unknown. Equal amounts of glucosamine hydrochloride and chondrosamine hydrochloride give rise to colours identical in tint and intensity. Under the specified conditions the accuracy of the determination is not affected by the presence of glucose, galactose, fructose, arabinose, glycine, alanine or histidine; tryptophane has no effect, as the tryptophane reaction with Ehrlich's reagent requires a greater concentration of acid. Many carbohydrates and amino-acids also interfere in more highly acid solutions. Although 1-aminoglucose is not known to occur naturally, and is, therefore, unlikely to be present in the products of the acid hydrolysis of either gluco-proteins or nitrogen-containing polysaccharides, this aminohexose condenses readily with acetylacetone, and, under the experimental conditions described for glucosamine and chondrosamine, yields a coloured solution almost identical in tint and intensity with that produced by equal quantities of these compounds. The new method is more satisfactory than the colorimetric method for the determination of glucosamine recently described by Zuckerkandl and Messiner–Klebermass (*Biochem. Z.*, 1931, **236**, 19), since it avoids the process of evaporation to dryness and subsequent conversion of the glucosamine into its *N*-monoacetyl derivative. P. H. P.

Colorimetric Determination of Vitamin *A* by the Alkali Digestion Method. A. W. Davies. (*Biochem. J.*, 1933, **27**, 1770–1774.)—A simplified form of the alkali digestion process for the assay of vitamin *A* in tissues by the colorimetric method has been devised. The method was first adopted by Rosenheim and Webster (*Biochem. J.*, 1927, **21**, 111), and was used upon samples of human liver obtained at autopsy by Moore (*Lancet*, 1932, ii, 669). The new process permits of rapid working (it is possible to average 3 to 4 assays per hour), and gives results substantially in agreement with those obtained by the Soxhlet extraction method. The digest is given a preliminary shaking with a small proportion of alcohol, and then a single extraction with ether is sufficient to extract almost all (usually 90 per cent. or more) of the vitamin *A*. Two washings of the ethereal extract are sufficient to secure freedom from alkali, and, by adherence to the correct proportions of alcohol, ether and water, the formation of emulsions can be avoided except in rare instances. Details of the method are given. The effect of ageing on the stability of the vitamin has been studied, not with a view to ascertaining the ideal conditions for ensuring its stability, but in order to obtain information as to its behaviour under routine conditions involving periods of storage at ordinary temperatures, *e.g.* during transmission by post. It was found that at room temperature vitamin *A* deteriorates less rapidly in liver specimens treated with potash than in untreated tissues kept without preservative treatment. In the case of specimens of liver transferred immediately *post mortem* to potash solution, and then stored at room temperature, no serious decrease in vitamin *A* content is to be anticipated if the assay is carried out within 14 days of death.

P. H. P.

Grouping of Halibut Liver Oils. R. T. M. Haines and J. C. Drummond. (*J. Soc. Chem. Ind.*, 1934, 53, 81–82T.)—An extensive range of halibut liver-oils of known origin were examined shortly after their preparation, particularly in respect of their vitamin *A* "blue" values (calculated to refer to 0·2 ml. of a 10 per cent. solution) and iodine values. Previously the smaller range of oils examined were of very uncertain origin, and no obvious correlation was found in which the vitamin-content was concerned (ANALYST, 1933, 58, 356). The iodine values were determined by the method originally described by Rosenmund and Kuhnhenn, using pyridine sulphate bromide as halogenating agent. The oils were from three districts, West Greenland, "Labrador," and East Greenland and Faröe. When the iodine values were plotted against the blue values, the points representing West Greenland oils fell on a smooth curve, and in cases where the vitamin *A* values were below about 2000 blue units the graph was sensibly a straight line, curvature becoming apparent only when the actual bulk of vitamin was appreciable. Since the range of blue values of the "Labrador" (*a*) and East Greenland and Faröe oils (*b*) was limited, (*a*) 325 to 730, and (*b*) 558 to 1700, the effect for these oils was not so striking, but in each case the points were grouped about a line. Iodine values corresponding to zero blue values were 112·5 for West Greenland, and 123·25 for Faröe oils, and it is suggested that East Greenland and Faröe oils are distinguished from West Greenland oils by their higher values for the ratio iodine value/blue value, at least for the 1933 season. The range of blue values for West Greenland oils was 523 to 4350, and iodine values 116·9 to 161·0; for "Labrador" oils, 325 to 730 and 116·2 to 121·5; and for East Greenland and Faröe oils 558 to 1700 and 124·5 to 135. A further examination of a Danish, 2 Norwegian and 4 American oils gave figures so completely different (except in one case) from those for the authentic samples, that blending of cod-liver oils and halibut oil was suspected and a table is given showing the blue and iodine values for various mixtures of this kind.

D. G. H.

Standardisation of the Antiscorbutic Potency of Ascorbic Acid. L. J. Harris and S. N. Ray. (*Biochem. J.*, 1933, 27, 2016–2021.)—Results are published which confirm conclusions given in an earlier note by Harris and Ray (ANALYST, 1933, 58, 489). Assays by the tooth protection method, on large numbers of guinea-pigs, and with ascorbic acid and orange juice always given simultaneously at various identical levels of potency, show consistently that the activity is such that 2 mgrms. of ascorbic acid are equivalent to 3 ml. of orange juice, or, that the minimum dose for full tooth protection (under the conditions of the test) is 2 mgrms. This value agrees with the amount of ascorbic acid actually present in average specimens of orange juice, or in "good" lemon juice, as determined by titration (0·6 to 0·7 mgrm. per ml.). The authors state that their use of orange juice as a secondary or derived standard, in place of lemon juice used direct as primary standard, may be criticised, but they believe it to have some advantages. Lemon juice is subject to some variation in potency, so that the evaluation of ascorbic acid in terms of International Units will depend on the quality of the lemon juice used for comparison, but, taking the interpretation that the standard lemon juice means a "good" specimen, equivalent to the orange juice used in the test, and showing 0·6 to 0·7 mgrm. of ascorbic acid per ml. on titration, ascorbic acid has a potency of 15 International Units per mgrm. Against "average" lemon juice as purchased retail in Cambridge, having an ascorbic acid content of 0·47 mgrm. per ml., the calculated activity for ascorbic acid works out rather higher, *viz.* 21 International Units per mgrm. The alternative value, 7·4 units per mgrm., put forward by Key and Morgan (*Biochem. J.*, 1933, 27, 1030), would indicate an ascorbic acid-content of 1·35 mgrms. per ml. for lemon juice, which seems difficult to reconcile with the fact that the reducing titre rarely rises above a value equivalent to about 0·7 mgrm. Possible reasons for the lack of agreement are discussed. The earlier conclusion of the authors is confirmed, *viz.* that lemon juice is an unsatisfactory standard, and should be replaced by ascorbic acid. Different specimens of lemon juice had ascorbic acid contents varying from 0·19 to 0·69 mgrm. per ml.; average 0·47, with an average deviation of ±0·11. P. H. P.

Indophenol-Reducing Capacity and Vitamin *C* Content of Extracts of Young Germinated Peas. S. W. Johnson. (*Biochem. J.*, 1933, 27, 1942–1949.)—It has been known for a considerable period that, whilst many dried seeds are devoid of antiscorbutic activity, they acquire this property very readily on germination. Experiments were undertaken to ascertain whether a quantitative relationship exists between the indophenol-reducing capacity and antiscorbutic activity of extracts of peas in the early stages of germination, and, also, if no such relationship exists, whether this is due to the presence of an active oxidised form of the vitamin in the young seedling. A number of extracts were prepared from peas germinated for 3 days, and both their indophenol-reducing capacities and their antiscorbutic activities were determined. The extracts with even the highest indophenol-reducing capacity were found to possess only half the antiscorbutic activity of the germinated peas from which they were obtained. Aqueous, phosphate and cyanide-phosphate extracts were found to be less active antiscorbutically than would have been expected if their indophenol-reducing capacity had been entirely due to ascorbic acid. All extracts from the germinated peas contained at least one substance other than ascorbic acid which reduced indophenol. No evidence was obtained that the active oxidised form of the vitamin was present in the early stages of germination. The ungerminated peas, which showed no antiscorbutic activity when tested in quantities of 2·5 grms., gave extracts which also reduced indophenol, though at a rather slower rate than ascorbic acid. It is evident, therefore, that the indophenol-reducing capacity of extracts is no true index of the antiscorbutic potency of the seedlings from which they were obtained, and that the formation of the active oxidised form of the vitamin during the early stages of germination is unlikely; it seems that the activity of the peas is due entirely to the reduced form of the vitamin. The fact that the extracts were less active than the peas from which they were prepared can best be explained on the grounds that it is not possible, by the methods used, to extract the vitamin completely. This shows the ease with which misleading results may accrue from testing extracts instead of tissues. If a part of the vitamin is bound to inhibiting substances, as suggested by Euler, it would seem most probable that such a complex would be insoluble or otherwise inextractable. P. H. P.

Vitamin *C* Content of Canned Tomato Juice. R. G. Daggs and A. G. Eaton. (*Ind. Eng. Chem.*, 1934, **26**, 292–295.)—The vitamin *C* content of commercial tinned tomato juice, estimated by Höjer's method of examining sections of the teeth (*Brit. J. Exptl. Path.*, 1926, **7**, 356), is only very slightly lower than that of the fresh juice. W. P. S.

Reactions of Terpenes with Antimony Trichloride. V. E. Levine and E. Richman. (*Biochem. J.*, 1933, **27**, 2051–2054.)—Various workers have shown that antimony trichloride in chloroform solution yields colour reactions with fish-liver oils and fish-liver oil concentrates, with carotenoid pigments, with certain sterols and their derivatives, and with certain five-membered monoheterocyclic compounds. Since unsaturation and the terpene groupings are common chemical factors in carotenoid pigments, in vitamin *A* and in sterols occurring in the plant and animal organism, the authors have studied the antimony trichloride reaction (Carr and Price reagent) on over thirty compounds of the terpene group. The reagent was tested on solutions of the terpenes in chloroform, and also on solutions of the terpenes in chloroform to which acetic anhydride had been added; the acetic anhydride prevents the formation of precipitates in the reaction mixture, and induces a more vigorous reaction and a more intense display of colour changes. The results, which are tabulated, show that the reaction is usually characterised by a succession of colour changes; in many cases the final colour is purple. Citral, in the presence of acetic anhydride, changes from dark yellow to brown, to wine red, to purple and, finally, to dark blue. Ionone, which may be obtained by the oxidation of carotene and of vitamin *A*, gives with antimony trichloride an amber colour changing to wine-red, and, finally, on long standing, to purple. In the presence of acetic anhydride the initial colour is amber, which changes to greenish-amber, mahogany-brown, and, finally, to reddish purple. Vogel and Stohl (*Ber.*, 1933, **66B**, 1066) converted β-ionone by cyclisation with sulphuric acid into an orange-yellow powder, which gave with antimony trichloride in chloroform solution a permanent and very intense blue colour with a maximum absorption spectrum at 510*mμ*, and a large band beginning at 430*mμ*. The following compounds yield no colour reactions: *dl*-camphor, *d*-camphoric acid, *d*-camphoric anhydride, *d*-camphorsulphonic acid and *l*-menthol. The following react very slowly and very slightly: *d*-camphor, borneol and *l*-menthone. The terpenes that react most vigorously are the unsaturated ones, and the higher the degree of unsaturation, the greater the reactivity of the compound. The presence of an aldehyde, alcohol or ketone group induces greater reactivity in the unsaturated compound. The camphane group is the least reactive, and the olefine group the most reactive. P. H. P.

Agricultural

Rapid Determination of Small Quantities of Lime in Soil Solutions. H. Beutelspacher. (*Z. anal. Chem.*, 1934, **96**, 161–172.)—The process is based upon the precipitation of calcium by a known amount of sodium tungstate and colorimetric determination of the excess of tungstate with titanous chloride. One ml. of solution (maximum content, 0·16 mgrm. CaO) is treated in a basin with 1 ml. of sodium tungstate solution (1·0487 grm. per litre; 1 ml. ≡ 0·2 mgrm. CaO), and evaporated to dryness on a water-bath. The residue is extracted with 2 ml. of distilled water; the insoluble part is rubbed and detached with a rubber-tipped glass rod, and the whole is transferred to a pointed tube and centrifuged for several minutes. One ml. of clear supernatant solution is transferred to a small tube and treated first with 0·2 ml. of 0·1 *N* hydrochloric acid, then with 1 ml. of titanous chloride solution (1 ml. of this is equivalent to 2 mgrms. of iron, as determined by titration of a standard ferric chloride solution in presence of thiocyanate). The blue colour can be matched at once against that produced by titanous chloride in the standard tungstate solution. Standard and assay should not deviate more than 30 per cent. The colour is stable for 2 to 3 hours; 50 determinations can be carried out together in about 2 hours. The normal inorganic constituents of soil solutions do not interfere. W. R. S.

Organic Analysis

Determination of Formaldehyde and Sulphites by Acidimetry. M. Malaprade. (*Compt. rend.*, 1934, **198**, 1037–1039.)—Since a rapid reaction occurs between formaldehyde and a neutral sulphite when one or other is present in excess, and the resulting formol-bisulphite combination is neutral in the presence of phenolphthalein and thymolphthalein, either substance may be determined by titrating the liberated sodium hydroxide. Thymolphthalein changes from colourless to blue at a p_H of 9·5 to 10·5. *Formaldehyde.*—The sample is first neutralised to the turning point of thymolphthalein, an excess of a neutral solution of sulphite (prepared by neutralising a solution of bisulphite) is then added, and the liberated sodium hydroxide is titrated until the indicator becomes colourless. It is not necessary to exclude air. *Sulphite.*—The sample is neutralised as before (but out of contact with air), excess of formaldehyde solution is added (itself first neutralised), and the liberated sodium hydroxide is titrated in air until the indicator is colourless, when phenolphthalein is added, and the titration is continued until the solution is colourless. It is possible thus to determine sulphites in the presence of hyposulphites, which have no action on formol, and also the free sulphur in rongalite. The titration of free alkali may conveniently be carried out with acetic acid containing sodium acetate, in order to eliminate local reactions due to the presence of strong acids. D. G. H.

Determination of Hydroxyl Groups in Alcohols and Phenols by Benzoylation in Tetrahydronaphthalene Solution at High Temperatures. T. M. Meijer. (*Rec. Trav. Chim. Pays-Bas*, 1934, **53**, 387–397.)—This method is based on determination of the hydrochloric acid liberated when an alcohol or phenol is treated with benzoyl chloride or one of the nitrobenzoyl chlorides. Tetrahydronaphthalene is used as a solvent for the reacting compounds, as its high boiling-point (205° C.) renders the use of sealed tubes unnecessary. A stream of air or hydrogen, free from carbon dioxide, is passed through a wash-bottle containing sulphuric acid, and then through the solution of alcohol (or phenol) and benzoyl chloride contained in a flask heated in an oil-bath. The gas proceeds upwards through a reflux condenser, and then through an absorption bottle containing water and afterwards through another charged with silver nitrate solution. The contents of the first of these absorption bottles are afterwards titrated with 0·1 *N* sodium hydroxide solution in presence of methyl red.

When benzoyl chloride was used, the percentages of the theoretical amounts of hydrogen chloride liberated from different hydroxyl compounds were: resorcinol, 94; quinol, 90·6; catechol, 84·6; benzyl alcohol, 90·4; cyclohexanol, 103·3; benzoin, 101·3; propyl alcohol, 84; isopropyl alcohol, 100; glycol, 62; glycerol, 48·2. With *p*-nitrobenzoyl chloride, the figures were: phenol, 101·6; *β*-naphthol, 94·9; resorcinol, 91·3; quinol, 92·3; catechol, 74; benzyl alcohol, 102·3; benzoin, 88·3; cyclohexanol, 101; 1 : 2-methylcyclohexanol, 97·3; 1 : 4-methylcyclohexanol, 96; propyl alcohol, 102·4; isopropyl alcohol, 105. With *m*-nitrobenzoyl chloride: quinol, 100; resorcinol, 107; catechol, 84·2; benzyl alcohol, 100. T. H. P.

Rapid, Accurate Determination of Acetone. Application to Biological Liquids. R. Gros. (*J. Pharm. Chim.*, 1934, **126**, 214–220.)—The precipitation of acetone by Nessler's reagent (*cf.* Bougault and Gros, ANALYST, 1922, **47**, 405) may be used for the accurate determination of acetone. The reagent is prepared in two parts: (A) 13·55 grms. of mercuric chloride and 36 grms. of potassium iodide are dissolved in water to 250 ml. (B) 540 grms. of sodium hydroxide are dissolved in water to 1 litre; 2 volumes of (A) and 1 volume of (B) are mixed immediately before use. The acetone is distilled off under a vacuum from a 250-ml. Erlenmeyer flask heated on a boiling water-bath, and is absorbed in the reagent contained in a special absorption pipette. The distillation occupies about 15 minutes, after which the flask is cooled and then again heated for 15 minutes and cooled. The vacuum is then released and the precipitate formed is washed several times (until free from chloride), either in the bulb of the pipette or in a centrifuge tube, the wash-water being poured through a weighed filter-crucible (1G4 or 2G4), in which the precipitate is ultimately collected and washed, under suction, with alcohol and then with ether. The weight of the precipitate, dried at 100° C. to constant weight, is multiplied by 0·0325 to obtain the weight of acetone.

To determine acetone in urine, 5 ml. of the urine are mixed in a 50-ml. flask with 1 ml. of basic lead acetate solution and about 20 ml. of water. After 1 to 2 minutes, 10 drops of dilute sulphuric acid (1 : 10) are added, and the solution is made up to 50 ml. with water, mixed and filtered. Alkaline urines should be neutralised with hydrochloric acid prior to the defecation. Of the clear filtrate, 5 ml. are used, as described above, for the determination of the acetone. When blood is to be tested, defecation is effected by treatment with an equal volume of 20 per cent. trichloroacetic acid solution. Check determinations have given satisfactory results. T. H. P.

Use of 2,4-Dinitro-phenylhydrazine as a Quantitative Reagent for Carbonyl Compounds. I. Benzaldehyde. R. E. Houghton. (*Amer. J. Pharm.*, 1934, **106**, 62–64.)—A rapid, simple, economical and accurate method for the determination of benzaldehyde is proposed by means of 2,4-dinitrophenylhydrazine. The benzaldehyde (0·1 grm.) is dissolved in 5 ml. of ethyl alcohol, diluted with 50 ml. of water, and to this is slowly added, with constant stirring, a reagent prepared by dissolving 0·25 grm. of 2,4-dinitrophenylhydrazine in 2·5 ml. of concentrated sulphuric acid and adding 50 ml. of water. The precipitate is stirred until it settles, and, after standing overnight, is filtered off on a tared Gooch crucible, washed with about 15 ml. of 2 *N* sulphuric acid, and then with water, until this gives no precipitate with barium chloride, and subsequently dried at 110° C. to constant weight. The stirring and digestion of the precipitate overnight are necessary to reduce occlusion of the reagent and to facilitate filtration. A series of ten duplicate determinations showed individual differences between 0·01 and 0·66 per cent. D. G. H.

Anti-oxygens of Fatty Oils. Action of *p*-Nitraniline. M. Nakamura. (*J. Soc. Chem. Ind. Japan*, 1934, **37**, 86B.)—The oxidation of oils with iodine values above 120 is accelerated by *p*-nitraniline to an extent nearly proportional to the iodine value. On oils with iodine values below 120, *p*-nitraniline begins to exert an anti-oxygen effect; this phenomenon of inversion takes place the more quickly, the lower the iodine values. Inversion of catalysis is correlated entirely with the iodine value, and not with any minor ingredient of the oil. R. F. I.

Oleic-Elaidic Acid Transformation as an Aid in the Analysis of Mixtures of Oleic, Linolic and Linolenic Acids. H. N. Griffiths and T. P. Hilditch. (*J. Soc. Chem. Ind.*, 1934, **53**, 75–81T.)—The quantitative conversion of higher monoethylenic *cis*-acids into their *trans*-(elaidic) forms, by means of the mercury and nitric acid reagent of Poutet in the proportions recommended by Archbutt (*J. Soc. Chem. Ind.*, 1886, **5**, 303), results in the production, at equilibrium point, of a product containing elaidic acid corresponding with 66 per cent. of the oleic acid originally present. This process has been applied to mixtures of acids. The procedure for the determination of oleic acid (as elaidic acid) in a mixture of fatty acids is to saponify the fresh oil, to recover the mixed fatty acids with minimum exposure to air, and to distil them as rapidly and as completely as possible at a pressure of 1 mm. or less, so as to obtain representative samples. The distilled acids (10 to 20 grms.) are shaken with mercury (0·2 to 0·4 grm.) and nitric acid (0·5 to 1 ml.) of sp.gr. 1·4 in a stoppered vessel immersed in water at room temperature for 1 hour, and, after standing overnight, the product is extracted with ether, and the solution is washed with dilute nitric acid and then with hot water. Water and ether are removed, the product is boiled with about 100 ml. of petroleum spirit, and the clear solution is decanted from the resinous material, which is washed two or three times with 20-ml. portions of petroleum spirit, the washings being added to the main solution. The solvent is removed, and the acids are submitted to the petroleum spirit and lead salt process. The solid acids obtained from the insoluble lead salts are again treated with petroleum spirit and re-submitted to the usual lead-salt procedure. From the yield and iodine value of the solid acids the quantity of elaidic acid is obtained, and therefrom the maximum percentage of oleic acid in the original mixed acids. The method was applied to the acids of olive, cotton-seed, tea-seed and ground-nut oils, in which oleic and linolic are the only unsaturated acids, and the proportions of oleic acid found were in each case in fairly close agreement with those obtained by the ester fractionation method. When oleic, linolic and linolenic acids were all present, as in linseed, hemp-seed, rubber-seed, walnut, soya-bean, and wallflower-seed oils, determinations were also made by the bromination and thiocyanogen methods (for which details of procedure are given). Values obtained by the elaidic process were in every case very close to those derived from the thiocyanometric analyses, but both were quite different from the corresponding figures deduced from the amounts of insoluble hexabromostearic acid isolated. The agreement was found to be so consistent that the elaidic method, when applied to the quantitative analysis of highly unsaturated oils, is regarded as an independent confirmation of the utility of the thiocyanometric method, but it is more intricate and tedious than the latter method. Due precautions are needed with these unsaturated oils to ensure complete attainment of normal equilibrium, and correct separation of the elaidic acid, and the particular behaviour of the individual unsaturated oils is given in detail (*cf.* ANALYST, 1934, 312). D. G. H.

Gelation of China Wood Oils (*Aleurites*) by Antimony Halides. T. François. (*Compt. rend.*, 1934, **198**, 1046–1048.)—If, drop by drop, the oil of *Aleurites Fordii* or of *Aleurites montana* is poured into a chloroform solution of antimony chloride, each drop immediately becomes a gel, but the oils of *Aleurites moluccana* and of linseed remain liquid; this reaction may be used for the identification of the oils and the detection of adulteration. Two ml. of a 10 per cent. solution of antimony trichloride in chloroform are placed in each of a series of test-tubes (12 × 14 × 160 mm.), and four drops of the sample of oil are added from a dropper, with constant stirring. With pure tung and montana oils, the mixture is coloured a caramel-brown, and total gelation is immediate. If 20 per cent. of foreign oil is present, gelation takes 1 or 2 minutes; if 40 per cent., 10 to 15 minutes, and the product is sticky, adhering to the sides of the tube. The degree of purity of an oil may rapidly be found with a minimum precision of 10 per cent. by making known additions of arachis oil, for example, and the amount of tung oil in a linseed oil may be found by determining how much of an authentic tung oil is needed to bring about gelation. Oils thickened by heating to the flash-point and rapidly cooled behave like the original oils from which they were derived. When studying the behaviour of mixtures of such thickened linseed and tung oils, 6 drops should be taken; gelation of the thickened tung oil takes 1 minute. D. G. H.

Inorganic Analysis

Nitrazine Yellow, a New Indicator. H. Wenker. (*Ind. Eng. Chem.*, 1934, 26, 350.)—Nitrazine yellow is 2,4-dinitrobenzene-azo-1-naphthol-3,6-disulphonic acid; in acid aqueous solution the colour is bright yellow, whilst the alkaline solution is deep blue. The colour-change takes place between p_H 6·4 and 6·8, with a sharp neutral point at 6·6. W. P. S.

2,3-Diaminophenazine as a Reagent for Metal Ions. T. Pavolini. (*Ind. Chimica*, 1933, 8, 692–694; *Ann. Chim. anal.*, 1934, 16, 123.)—A solution of 2,3-diaminophenazine gives a red precipitate with cupric and mercuric ions, which may be tested for as follows:—To the solution, neutralised to litmus, are added 10 to 20 drops of an alcoholic solution of 2,3-diaminophenazine hydrochloride (0·5 per cent.), the liquid is well shaken, and any red colour in the foam produced is observed. The sensitiveness is $1 : 1 \times 10^5$ for mercury, and $1 : 6 \times 10^6$ for copper. The compound may also be used as a drop reagent. Ammonium salts interfere when in concentration greater than 2 to 3 per cent. Iron interferes owing to the masking of the red colour by precipitated basic compounds. Bismuth, lead and cadmium yield yellow or orange-coloured precipitates, but these reactions are of low sensitiveness. S. G. C.

Analysis of Sodium Stannate Tin-plating Solutions. A. W. Hothersall, S. G. Clarke and D. J. Macnaughtan. (*J. Electrodepositors' Tech. Soc.*, 1934, 9, 118–121.)—The successful operation of alkaline sodium stannate tin-plating baths depends on controlling the free sodium hydroxide-content within narrow limits, maintaining a substantial concentration of quadrivalent tin, and avoiding the formation of bivalent tin in the solution. *Sodium Hydroxide.*—This may be titrated with acid after the addition of an excess of barium chloride, which precipitates as barium salts the interfering stannate and carbonate. Five ml. of the tin-depositing solution are transferred to a conical flask of about 400 ml. capacity, and 50 ml. of barium chloride solution (10 per cent.), and 1 drop of thymolphthalein indicator solution (1 per cent. in ethyl alcohol) are added. The suspension is titrated with standard hydrochloric acid (0·1 *N*), with vigorous shaking, until the blue colour produced by the thymolphthalein begins to be discharged. A further 1 drop of indicator is then added, and the titration is continued. The end-point is taken when the colour changes from a definite blue to practically white; this occurs comparatively sharply over a range of a few tenths of 1 ml. of titrating acid. One ml. of 0·1 *N* hydrochloric acid = 0·004 grm. of sodium hydroxide. *Colorimetric Method for Quadrivalent Tin.*—A rapid approximately quantitative method has been devised, suitable for works control, based on the production of a yellow turbidity of stannic iodide in 1 : 2 sulphuric acid, which can be compared colorimetrically. The method is applicable to amounts of tin from 0·0001 to 0·001 grm. A 0·1-ml. sample of the tin-depositing solution (containing about 10 to 100 grms. of tin per litre) is taken by means of a capillary-bore pipette, and diluted to 10 ml. with 1 : 2 sulphuric acid (a mixture, cooled to room temperature, of 1 vol. of concentrated sulphuric acid with 2 vols. of water). Into each of two test-tubes of the same dimensions (approximately 20 ml. capacity), marked "1" and "2," and each provided with a glass stirring-rod, are placed 0·5 ml. of potassium iodide solution (20 per cent.) and 9 ml. of cold 1 : 2 sulphuric acid, and the solutions are well mixed. Into tube 1 is run 1 ml. of the diluted sample, and the whole is mixed by stirring. Without delay, standard stannic sulphate solution (see below) is run from a small burette into tube 2, in small quantities at a time, with stirring, until a yellow turbidity similar in degree to that present in tube 1, is produced. The comparison is best made by holding the tubes close together in the hand, and observing them at a distance of some 15 inches or more from the eyes; it further aids in a satisfactory comparison if the relative position of the tubes is reversed a few times during the observation; before the final comparison is made, the volumes should be made the same by the addition of 1 : 2 sulphuric acid. When the turbidities match, the amount of tin added to tube 2 is equal to that present in tube 1. The standard stannic sulphate solution is prepared by dissolving 1 grm. of metallic tin in 50 ml. of concentrated sulphuric acid by heating, boiling for a few minutes to ensure the oxidation of the tin, cooling, diluting with two parts by volume of water, again cooling, and, finally, diluting to 1 litre with 1 : 2 sulphuric acid (1 ml. ≡ 0·001 grm. of tin). It is noted that (*a*) the comparison should be carried out as rapidly as possible, as the turbidity gradually changes in appearance, owing to the growth of particles, etc., and iodine is slowly liberated; (*b*) both stannic and stannous sulphates give similar yellow turbidities; (*c*) the turbidity is prevented from forming in the presence of chloride, partially or completely according to the amount present; (*d*) the turbidity decreases to nil as the sulphuric acid concentration is reduced. *Other Methods.*—Other methods include the accurate determination of quadrivalent tin by reduction with hypophosphorous acid and subsequent titration with iodine (Evans, ANALYST, 1931, 56, 171), determination of bivalent tin by titration with iodine, and determination of carbonate by Hepburn's method (ANALYST, 1926, 51, 662).

S. G. C.

New Reaction of Triethanolamine with Cobalt Salts. F. Garelli and T. Tettamanzi. (*Ind. Chimica*, 1933, **8**, 577–578; *Ann. Chim. anal.*, **1934**, **16**, 129.)—The addition of a few drops of cobalt chloride solution (5 per cent.) and a little ammonia to an aqueous solution of triethanolamine yields a violet-red colour with as little as 0·5 part of triethanolamine per 100,000. Conversely, triethanolamine may be used to detect cobalt; small amounts of nickel do not interfere.

S. G. C.

Interference of Nitric Acid in the Permanganate Titration of Iron. D. Totoiescu. (*Z. anal. Chem.*, **1934**, **96**, **183–188**.)—The author observed that the presence of nitric acid in the permanganate titration of iron, when reduction zinc and sulphuric acid has been used, leads to high results; the nitric acid is reduced to a large extent to hydroxylamine, which consumes permanganate. Hence, if nitric acid has been introduced, it should be entirely removed by evaporation with sulphuric acid practically to dryness. If necessary, the evaporation should be repeated. The titrated liquid should give a negative reaction with diphenylamine. W. R. S.

Detection of Small Quantitities of Tantalum and Niobium. W. R. Schoeller. (*Z. anal. Chem.*, 1934, **96**, 252–257.)—The precipitation of the coloured tannin complexes is recommended for the identification of tantalum and niobium in small quantities of minerals; the reaction is shown to be more sensitive, specific, and convenient than those proposed by Rienäcker and Schiff, *i.e.* hydrolytic precipitation of tantalic acid, and formation of a lake of niobium sesquioxide with alizarin (*Z. anal. Chem.*, 1933, **94**, 415). About 2 mgrms. of powdered mineral are fused in a small silica crucible with a speck of potassium bisulphate, and the melt is dissolved in 1 to 2 ml. of ammonium oxalate solution. The solution is treated at the boiling-point with about 0·1 grm. of ammonium chloride and 0·02 grm. of tannin (solid), and left for a short time. The yellow tantalum precipitate permits of the detection of 0·05 mgrm. of Ta_2O_5 per ml.; the niobium reaction (red precipitate) is approximately three times as sensitive. Iron does not interfere in the slightly acid oxalate solution. If the mineral contains titania (hydrogen peroxide test) it is fused with bisulphate, and the melt is extracted with 5 per cent. sulphuric acid containing one per cent. of tannin (ANALYST, 1929, **54**, 453); the coloured residue containing the earth acids may be tested, after ignition, by the above reaction. W. R. S.

Colorimetric Determination of Uranium in Low-Grade Ores. J. Tschernichow and E. Guldina. (*Z. anal. Chem.*, 1934, **96**, 257–263.)—The procedure is based on the coloration of uranyl ferrocyanide; the elimination of iron is effected by electrolysis with the mercury cathode. The ore (0·5 grm.) is gently boiled with 20 ml. of sulphuric acid (1 : 4) and 5 ml. of hydrochloric acid for 30 minutes. The filtered solution is precipitated with 5 ml. of 3 per cent. hydrogen peroxide and carbon dioxide-free ammonia. The washed precipitate is dissolved in very little hot 1 per cent. sulphuric acid, and the solution (maximum volume 50 ml.) is electrolysed with a mercury cathode at 4 to 5 amperes and 6 to 8 volts until the iron reaction with ferricyanide on a spot plate becomes negative. The electrolyte is precipitated with ammonia as before, the precipitate being washed and dissolved in 3 per cent. sulphuric acid. The solution is treated with ammonia until faintly cloudy, and cleared with a few drops of *N* sulphuric acid. The uranium is precipitated free from vanadium by 5 ml. of 6 *N* acetic acid and 15 ml. of *M*/3 disodium phosphate. If the amount of alumina present is small, a little alum solution (5 mgrms. of Al_2O_3) should be added. The solution is boiled, and filtered after 10 minutes, and the precipitate is washed 5 to 6 times with *N* ammonium nitrate solution. The phosphate precipitate is dissolved in hot 0·2 per cent. sulphuric acid, with which the solution is made up to 100 ml. Ten ml. of the solution are treated in a glass cylinder with 5 ml. of a 10 per cent. solution of potassium ferrocyanide containing 1 per cent. of sodium sulphite, and, after a few minutes, the tint is matched against those of a series of standard tubes containing

1, 2, 3, ... 7 ml. of a solution of uranium sulphate free from iron. This solution is prepared from one of uranyl nitrate of known strength by precipitation with ammonia, solution of the precipitate in 0·2 per cent. sulphuric acid, and adjustment of the concentration to 0·1 mgrm. of U_3O_8 per ml. by means of the same acid. A closer result is obtained by a second match of freshly-prepared unknown solution against a fresh scale of 3 tubes, the strongest and weakest of which correspond to the two neighbouring tubes of the first scale between which the unknown has been located, while the intermediate tube contains 0·5 ml. of standard uranium solution less than the stronger of the two. Residues and by-products containing organic matter must be ignited prior to the determination. W. R. S.

Microchemical

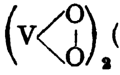
Micro-Iodimetric Determination of Iron. J. Straub. (*Mikrochem.*, 1934, 14, 251–255.)—Neumann's method (*Z. physiol. Chem.*, 1902–3, 37, 115; 1904–5, 43, 32) is found to give incorrect results for amounts of iron less than 0·05 mgrm. For amounts of iron from 0·5 to 0·01 mgrm. good results are obtained when 2 to 3 drops of concentrated hydrochloric acid are added to 8 to 9 ml. of the test solution and 1 to 2 grms. of potassium iodide, and the liberated iodine is titrated against *N*/500 sodium thiosulphate solution, with starch as indicator. Organic matter may be destroyed by ashing the material in a platinum crucible, treating the residue with 2 to 3 drops of hydrochloric acid, and adding 2 to 3 drops of perhydrol. After this mixture has been evaporated to complete dryness the residue is taken up in 2 to 3 drops of hydrochloric acid and transferred to the conical flask by means of 8 to 9 ml. of water, and the determination is carried out as before. Alternatively, the organic matter may be decomposed by adding fuming nitric acid and heating until a white residue is obtained; this is taken up in hydrochloric acid and the iron is determined as before. J. W. B.

Quantitative Micro-analysis of Uranites. F. Hecht and W. Reich-Rohrwig. (*Mikrochem.*, 1933, 12, 281–292.)—A scheme for the complete micro-analysis of uranite minerals is described for an initial weight of about 35 mgrms. The mineral is dissolved in nitric acid (1: 1), and filtered from the insoluble matter, which is ignited and weighed, and the silica is volatilised with hydrofluoric acid in the presence of sulphuric acid. The soluble silica in the filtrate is rendered insoluble by repeated evaporation with nitric acid and determined. The nitrates are then converted into chlorides, and hydrogen sulphide is passed through the solution to precipitate metals of the sulphide group. On treatment with yellow ammonium sulphide a very small trace of substance dissolves which is tabulated as SnO_2(?). The residue of lead sulphide (bismuth is normally absent) is dissolved in nitric acid, the solution is evaporated with sulphuric acid, and the lead is weighed as lead sulphate. The hydrogen sulphide in the filtrate is destroyed by evaporation to dryness and oxidation with a little nitric acid, and then iron, aluminium, thorium and the rare earths (including titanium and zirconium) are precipitated with ammonia in the presence of 0·6 to 0·7 grm. of hydroxylamine hydrochloride, and are thus separated from uranium, calcium and magnesium; this precipitation is repeated once or twice. In the combined filtrates the hydroxylamine and most of the ammonium salts are destroyed by evaporation with nitric acid. The precipitation with hydroxylamine is again repeated, the reagent is destroyed as before in the filtrate, and then uranium is precipitated as oxime in acetic acid solution, and finally weighed. The filtrate is evaporated, the residue is ignited, calcium is determined by precipitation with picrolonic acid, and finally magnesium is precipitated with sodium phosphate in the filtrate from the calcium, ignited to pyrophosphate and weighed as such, or converted into the oxime by precipitation with 8-hydroxyquinoline in alcoholic ammoniacal solution (Strebinger and Reif, *Mikrochem.*, *Pregl-Festschrift*, 1929, 319). The hydroxide precipitate of iron, aluminium, chromium and the rare earths is dissolved in nitric acid. Thorium and part of the rare earths are precipitated with malic acid, and filtered off, and the filtrate is treated with ammonia until the reaction is only weakly acid; the new precipitate of rare earths is filtered off, and both fractions are separately ignited and weighed as oxide. In the filtrate, after destruction of the oxalic acid, iron and aluminium are precipitated with ammonia and ignited and weighed as oxides. The oxides of thorium and the rare earths are brought into solution by treatment with pyrosulphate and then nitric acid, the first fraction is precipitated with ammonia and filtered off, the precipitate is dissolved in nitric acid, and in the combined solution of the nitrates of both fractions the thorium is separated from the rare earths, after removal of the acid, by conversion into the hydrated peroxide, by means of ammonium nitrate and hydrogen peroxide. The separation is repeated, and finally the precipitate is ignited and weighed as thorium dioxide.

The total sulphur is determined in a separate portion of the mineral, which is fused with ten times the amount of a mixture of sodium carbonate and sodium nitrate (3 : 2) in a porcelain crucible in an electric furnace. The melt is treated with water and filtered, and the residue is washed, first with water and then with 1 per cent. sodium hydroxide solution. Finally, the filtrate and washings are cautiously acidified with gaseous hydrogen chloride. The silica is separated by evaporation with hydrochloric acid, the uranium and aluminium in the filtrate are precipitated with ammonia (free from carbon dioxide), the liquid is filtered, the filtrate is acidified with hydrochloric acid, and the sulphate is determined as barium sulphate. The *apparatus* used comprised the following: Berlin porcelain crucibles of outside top diameter 33 mm., bottom diameter 19 mm., a height of 43 mm. and a capacity of 25 cm.; Emich filter-sticks, with porcelain filtering surface (Berlin Porzellan Fabrik); platinum crucibles, with a top diameter of 28 mm., bottom diameter 17 mm., height 40 mm., and capacity 20 ml.; platinum Neubauer filter-sticks (from Heraeus, Hanau); electrically-heated water-bath (author's design), with suction to aid evaporation (from P. Haack, Vienna). For gas-inlet a special cover-glass, with an inlet-tube passing through it, was used to avoid contamination. When the precipitates were to be weighed without ignition, filter-beakers were used (*Recent Advances in Analytical Chemistry*, Vol II, *Micro-Analysis*). A glass stand was used for the dropping pipettes, by means of which the liquid reagents were added. A number of analyses, in which the sum of the results ranges from 98·33 to 100·42 per cent., are cited. J. W. B.

"Spot" Tests for Hydrogen Peroxide. F. Feigl and E. Fränkel. (*Mikrochem.*, 1933, 12, 303–306.)—(i) *By formation of Prussian blue.*—A drop of the dilute solution under examination is mixed on a spot-plate with a drop of reagent (equal volumes of 0·4 per cent. ferric chloride and 0·8 per cent. potassium ferricyanide solution). An intense blue colour or precipitate indicates hydrogen peroxide. A blank must be carried out. The same reaction occurs with other reducing substances, such as stannous chloride, thiosulphate, nitrites, and sulphites. *Smallest amount detectable*: 0·08 γ of H_2O_2; *Limit of dilution*: 1:600,000.

(ii) *By decolorisation of the higher oxide of nickel.*—Hydrogen peroxide is catalytically destroyed by nickel hydroxide, and from higher oxides of nickel the divalent oxide or hydrated oxide is formed. The test depends on the disappearance of the black colour of the nickel hydroxide, which is used in admixture with barium sulphate in the form of a paste. A blank must be carried out. *Smallest amount detectable*: 0·01 γ of H_2O_2. *Limit of dilution*: 1:5,000,000. To make the paste, baryta water is mixed with bromine water, and the resulting barium hypobromite is mixed with nickel sulphate and warmed. The proportions should be such that a grey precipitate is formed. This is filtered off and washed and can be kept for a long time in a moist condition in a stoppered bottle.

(iii) *By formation of peroxo-vanadates.*—The test may be used either for the detection of peroxides or vanadates: The yellow peroxo-vanadate,  $\left(V\begin{smallmatrix}O\\|\\O\end{smallmatrix}\right)_2(SO_4)_3$, in converted into yellow ortho-peroxo-vanadic acid according to the equation: $(VO_2)_2(SO_4)_3 + 6H_2O \underset{H_2SO_4}{\overset{H_2O_2}{\rightleftharpoons}} 2(VO_2)(OH)_3 + 3H_2SO_4$. Thick filter paper ("spot" paper) is impregnated with a 1 per cent. alkali vanadate solution, slightly acidified, and dried. On adding a drop of peroxide solution, a yellow to rose-red fleck is formed. *Smallest amount detectable*: 3 γ of H_2O_2. *Limit of dilution*: 1:16,600.

(iv) *By reduction of gold salts.*—$2\,AuCl_3 + 3H_2O_2 = 6HCl + 2\,Au + 3O_2$. A drop of a 0·01 per cent. gold chloride solution is warmed in a micro-crucible with a drop of the hydrogen peroxide solution. A red or blue colour, due to colloidal gold, indicates the presence of a peroxide. *Smallest amount detectable*: 0·07 γ of H_2O_2. *Limit of dilution*: 1:714,000.

(v) *With alkali thiocyanate.*—About 1 ml. of a 5 per cent. solution of an alkali thiocyanate is acidified with sulphuric acid and warmed with a drop of the peroxide solution; according to the amount of peroxide present, a red-yellow precipitate or colour appears. *Smallest amount detectable*: 0·7 γ of H_2O_2. *Limit of dilution*: 1:71,000.

J. W. B.

Micro-Determination of Phosphorus as Phosphomolybdate. R. H. A. Plimmer. (*Biochem. J.*, 1933, 27, 1810–1813.)—The determination of phosphorus in organic matter by the volumetric determination of ammonium phosphomolybdate (a method in use since 1906) is accurate for quantities of phosphorus ranging from 1 to 30 mgrms. From 1914 to 1933 various workers have maintained either that the method is inaccurate for micro-quantities, or of no value for quantities below 0·1 mgrm. Greenwald (*J. Biol. Chem.*, 1913, 14, 369) and Taylor and Miller (*J. Biol. Chem.*, 1914, 18, 215), however, obtained satisfactory results with quantities of 0·015 to 0·12 mgrm. Pregl (*Quantitative Organische Mikroanalyse*), who weighed the precipitate, regarded the process as accurate, and quotes Lieb as proving the method applicable volumetrically to 0·03 mgrm. It is generally agreed that excellent results are given with quantities ranging from 0·1 to 10 mgrms., and the author has carried out an investigation to ascertain the reason for the general failure with the micro-quantities. He shows that the accurate determination of micro-quantities of 0·01 to 0·1 mgrm. of phosphorus by the molybdate method depends upon: (1) the conditions of precipitation; 20 ml. of 10 per cent. ammonium nitrate solution must be present for every ml. of concentrated sulphuric acid; (ii) the use of a purified solution of ammonium molybdate, such as that of Pregl; and (iii) the filtration of the precipitate on an asbestos filter such as that of Bertrand. For quantities above 1 mgrm. of phosphorus the perforated platinum plate is preferable. With the procedure described, four determinations can be made in 1 hour. The sensitivity of the precipitation of ammonium phosphomolybdate under the described conditions has been tested qualitatively. Quantities of phosphorus from 0·009 to 0·006 mgrm. in about 25 ml. began to come down in 2 to 3 minutes; from 0·005 to 0·003 mgrm. in 6 to 12 minutes; 0·002 mgrm. showed on standing 1 hour, and 0·001 mgrm., which was just visible but quite evident on filtering on to the asbestos, in 1½ hour. The micro-method is applicable to solutions of inorganic phosphate and to all forms of organic phosphorus for determination of total phosphorus. Inorganic phosphate in the presence of phosphoric esters not rapidly hydrolysed by acid, such as are present in blood-filtrates, can be determined, especially if filtration is carried out after 15 minutes, or if the precipitation is allowed to proceed at room temperature overnight. P. H. P.

Physical Methods, Apparatus, Etc.

Nickel Salts as Light Filters. W. V. Bhagwat. (*J. Indian Chem. Soc.*, **1934, 11,** 5–11.)—The limits for the transmission of light by nickel sulphate solutions are as follows:

Concentration	Range of transmission mμ	Max. transmission Per Cent.
5·28 *N*	440–620	53·7
2·3 *N*	400–680	79·4
0·9 *N*	All	89·1

Nickel salts, when used in combination with cobalt salts, transmit solely in the ultra-violet region, and, therefore, form suitable light filters for ultra-violet photography.

Salt	Time of exposure Hours	Transmission	
		Visible mμ	Ultra-violet mμ
(i) 2·08 *M* nickel sulphate + 1·83 *M* cobalt chloride; each in 1 cm. quarter cell	4	560–630	330·7–359·8
(ii) 4·16 *M* nickel nitrate + 3·66 *M* cobalt chloride	4	Nil	342·0–352·7 (faint)
(iii) 2·08 *M* nickel nitrate + 3·66 *M* cobalt chloride	4	Nil	330·7–359·8
(iv) 3·66 *M* cobalt chloride	4	710–760	261·4–406·3

Reviews

AN INTRODUCTION TO BIOCHEMISTRY. By Prof. W. R. FEARON, M.A., Sc.D., M.B., F.I.C. Pp. x + 313. London: William Heinemann (Medical Books), Ltd. 1934. Price 10s. 6d. net.

Perhaps the most startling thing about this book is the opening sentence of the Preface, which reads "I have sought to approach the living organism, and to lead such as may be disposed to follow me, along the less worn path of *inorganic biochemistry*." Professor Fearon, whose volume is dedicated to Sir Frederick Hopkins, and therefore raises in the reader expectations of a very high standard, has been compelled by the unfairness of nature, which insists upon being much more organic than inorganic, to depart from the more startling implications of his introductory fanfare.

Chapters I, II and III, on The Subject Matter of Biochemistry, The Biological Elements, and Inorganic Compounds, respectively, give place to a series of chapters on the various well-recognised groups of organic substances, right up to Chapter XIX on Autacoids, a somewhat unusual term coined by Schaefer to replace "internal secretion" or "hormones."

It can be said at once that the book is packed with information, well arranged and set up, and substantially free from serious errors of fact or typography. It is clearly written, with the advanced student primarily in mind, but this will not prevent its being one of the best summaries of modern biochemistry for the use of analytical and other practising chemists.

Other reviewers have already commented on the fact that this book, published early in 1934, has succeeded in bringing the story of biochemistry almost up to the end of 1933. In the course of this achievement, however, a few slips have clearly proved unavoidable. For example, the careful student is likely to be puzzled by the consecutive attribution to ergosterol of the formulae $C_{27}H_{41}OH$ (p. 129), and $C_{28}H_{44}O$ (p. 130); the latter is, of course, in accordance with modern views. Also Dr. Fearon seems to be a little at sea about the correct use of the symbol "λ"; he appears to think it interchangeable with $m\mu$.

The up-to-date and complete scope of this book is exemplified by the inclusion of references to several important recent pieces of work, such as that on the common chrysene nucleus of many substances of physiological action, the synthesis of certain carcinogens (though no mention has been found of the fact that some are also oestrogenic), the identification of vitamin *C* with ascorbic acid (though not its synthesis).

In the excellent chapter on Food and Vitamins no space is given to one very important pharmacological principle, namely, the use of international standard preparations as unit substances, to avoid the difficulties that arise in assays when an attempt is made to use some "unit" of animal reaction. There is a great deal of confusion still on this point, and a failure to distinguish between the existence of an international unit and an international standard preparation; the sooner students are made to understand the position clearly, the better for everybody.

If, as is to be hoped, Professor Fearon finds himself soon called upon for a new edition of this book, he would be well advised to include therein some reference to the increasing use of spectroscopic methods in biochemical work; a reference to the recent introduction of the so-called chromatographic analysis might also not be out of place.

A. L. BACHARACH

FUNDAMENTALS OF BIOCHEMISTRY. T. R. PARSONS, B.Sc., M.A. Fourth Edition. Pp. xii + 436. Cambridge: W. Heffer & Sons, Ltd. 1933. Price 10s. 6d. net.

The author's aim in this edition, as in the first edition of 1922, has been to give students new to the subject an introductory account of the more important biochemical aspects of human physiology. It may be said at once that the book represents a real accomplishment, for, with only an elementary knowledge of organic chemistry, a student will be able to follow the author readily throughout the course he has set, and not less because of his very readable style. Perhaps in the desire to make his book an entrancing "story rather than a catalogue," the author has been led into some curiosities of expression not usually found in a scientific text-book, as on p. 125, for example, where he refers to saponification thus: " . . . if we take an ester and stew it up with caustic soda . . . " But this is by the way.

To others besides the student, this book will be found interesting and refreshing. To the chemist generally, and particularly to one who is interested in the constituents of foodstuffs and their fate in the body, it is a stimulating treatise, though small, and modest in its aim. It gives a clear and concise account of our newer knowledge on the constitution of the proteins, and on vitamins, enzymes, and body-pigments.

In the Chapter on "Fats and their Metabolism," the interesting statement is made (p. 131) that "a foreign fat fed to a lactating animal may appear in its milk." Put baldly in this way, it might be taken to involve serious difficulties to the analyst in the examination of milk and milk products, but few would be found to affirm that there is in practice any real difficulty due to such a cause. On p. 337, the strength of a sodium chloride solution isotonic with mammalian blood is given as 0·95 per cent., instead of the usual 0·85 per cent.

In the Chapter (XII) on "The Human Machine," the author gives in some 40 pages a thoroughly adequate summary of our knowledge of the fuel requirements and energy output of the human body that can be recommended to all interested in this fascinating subject.

The book as a whole has impressed the reviewer with its value both to the student and to the food chemist. Each chapter is succeeded by a short summary and bibliography, and there is a good index. The type and general make-up of the volume are excellent.

ARNOLD R. TANKARD

QUALITATIVE CHEMICAL ANALYSIS. By ROY K. MCALPINE, Ph.D., and BYRON A. SOULE, Sc.D., University of Michigan. Based upon the text of A. B. Prescott and O. C. Johnson. Pp. xii+697. London: Chapman & Hall, Ltd. 1933. Price 21s. net.

The sub-title of this book states that it gives "Certain Principles and Methods used in identifying Inorganic Substances, together with a systematic Survey of the Chemistry of these Materials." Like some other transatlantic books on the subject, it is written expressly (sometimes a little too obviously) for college tuition—as shown in passages such as the following: "in order that a fair range of ground may be covered in a single semester it is necessary that the scheme of analysis be fairly simple" (p. 6).

The text-matter comprises 145 pages of theoretical considerations, 285 closely-printed pages on the chemistry and reactions of metals, 138 pages on the non-metals, and 38 pages on the systematic examination of unknown substances. The copious appendix includes a chapter on the balancing of equations. Numerous footnotes on almost every page refer to the most recent original literature. The analytical and general chemistry of the commoner elements is treated with a wealth of detail which raises a doubt as to whether this type of book is suitable as an introduction to analytical chemistry. The student is advised "to browse through" this massive tome; but, considering the short time put at his disposal in the curriculum, one may perhaps be allowed to wonder whether the average freshman can do more than nibble at this heavy fare without serious risk of mental indigestion. Rightly or wrongly, I believe that the learner should be introduced to the subject through more concise and elementary manuals, as generally used in British and Continental training institutions. Such preliminary survey of the whole field will enable those who desire to specialise in chemistry readily to take up a more advanced and detailed study of their principal subject.

As regards the common elements, the book is a reliable compilation of a multitude of facts and observations, and as such will be useful to inorganic and to analytical chemists. A few disputable statements were noticed, *e.g.* that cobalt "may be weighed as the cobaltinitrite" (p. 337), and that precipitated nickelic oxide has the formula $NiO_2.nH_2O$ (p. 343). The rarer elements are treated more succinctly, and the information is not always accurate. Two instances may be given. The table of the reactions of the platinum metals (p. 281) reproduces that in Newton Friend's Textbook (Vol. IX, 1920) with the inaccuracies I pointed out in the following passage when reviewing that work: "the yellow precipitate of potassium chloroplatinate has not been included; the yellow precipitate produced by dimethylglyoxime is attributed to ruthenium instead of palladium, whilst palladous chloride is wrongly stated to give a red precipitate of K_2PdCl_4. As a matter of fact, the chloropalladite, K_2PdCl_4, is readily soluble in water, whilst the red chloropalladate, K_2PdCl_6, is not."

The above is a case of uncritical reproduction of inaccurate statements. In the next instance the authors have committed a serious error in quoting from the original literature. In a brief mention of Powell and Schoeller's tannin process for the separation of tantalum from niobium, they make the following statement: "The tantalum precipitate is light brown in color; if contaminated with Cb it is red" (p. 377). It seems hardly possible that anybody could have read the directions and yet missed the vitally important point, emphasised throughout the paper, that the pure tantalum precipitate is sulphur-yellow. Contamination with niobium produces an orange-coloured precipitate; a brown tantalum precipitate is produced only in presence of titanium or tungsten. W. R. SCHOELLER

NACHWEIS DER BIOLOGISCH WICHTIGEN KÖRPER DURCH FLUORESZENZ UND FLUORESZENZSPEKTREN. By CHARLES DHÉRÉ. Handbuch der biologischen Arbeitsmethoden. Edited by EMIL ABDERHALDEN. Section II, Physikalische Methoden, Part 3, No. 4. Pp. 3097 to 3306. Berlin and Vienna: Urban and Schwarzenberg. 1933. Price RM. 11.50.

"Abderhalden" has long joined the ranks of those publications which seem never to be completed, and its ramifications have led us into many unfamiliar backwaters of experimental biology. It is safe to speculate, however, that the present volume on the applications of fluorescence methods was not contemplated when the series was started several years back, since the development of the subject has been mainly during the last five years, and, indeed (apart from general matters of technique), a reference dated previous to 1928 is a rarity.

The book, which is well-illustrated, is divided into two almost equal portions, dealing with apparatus, technique and the physical chemistry of fluorescence phenomena, and with applications of the method, respectively. The first may, therefore, be read independently of any biological interests, and is an excellent account of the usual methods of generating ultra-violet light. Certain of the sources apparently available on the commercial scale in Germany, are of particular interest, and special mention may be made of the cadmium-vapour lamp. Vertical illuminators for microscopes which can be used with ultra-violet light are quite an innovation in fluorescence microscopy, and their inclusion is an indication of the general up-to-date standard of the book. Spectroscopical analysis of fluorescence is, of course, almost an essential feature of work connected with substances of biological interest, and here again descriptions and illustrations are given of the most recent apparatus. Strangely enough, the mercury-in-quartz lamp, which many workers have learned to regard as the most convenient source of ultra-violet light for fluorescence analysis, receives only scant attention, and one is left with the impression that this general opinion is, perhaps, not shared by the author.

The physico-chemical chapter is of distinct academic interest, but it is to the sections on the applications of the method that biological workers and analysts will turn with most interest. The former, at any rate, will not be disappointed, for they will find recorded masses of data, chiefly of a spectroscopical nature, and numerous observations which probably are more of importance as an aid to elucidating structures than as methods of actual detection. As might be expected, considerable attention is devoted to the proteins, and, in particular, to the fluorescence of porphyrin and chlorophyll, on which the author is probably the foremost authority, and certainly the most prolific worker.

Carbohydrates, fatty substances and alkaloids are also dealt with shortly, but the information throughout is rather of an academic character, and there is little in it to assist the average analyst, whose equipment seldom consists of anything more elaborate than a mercury lamp, and who has no facilities for fluorescence spectroscopy. Thus, for example, insufficient stress is laid on the importance of standardised conditions, particularly of details, in carrying out work of this type, although (probably for this reason) the observations recorded with certain alkaloids are at variance with those obtained by other workers; the usefulness in this connection of capillary analysis might also have been emphasised.

At the same time, there is no claim that the volume is intended as a laboratory handbook for the general analyst, and it can certainly be unreservedly recommended to the specialist as the fullest account obtainable of the application of fluorescence methods to biological work.

JULIUS GRANT

Publications Received

COMPREHENSIVE TREATISE ON INORGANIC THEORETICAL CHEMISTRY. Vol. XIII. IRON, Part II. By J. W. MELLOR. Pp. 948. London: Longmans, Green & Co. 1934. Price 63s. net.

CONDUCTOMETRIC ANALYSIS. By H. T. S. BRITTON. Pp. 178. London: Chapman & Hall. 1934. 12s. 6d. net.

PHYSICO-CHEMICAL PRACTICAL EXERCISES. By W. N. RAE and J. REILLY. London: Methuen. Price 7s. 6d. net.

SOIL ANALYSIS. By C. H. WRIGHT. London: T. Murby & Co. 1934. Price 12s. 6d. net.

AAN P. VAN DER WIELEN. (A Collection of Papers on Chemical and Pharmaceutical Subjects, published by Members of a Committee in recognition of the work of Professor van der Wielen, 1909–1934.) Amsterdam: D. B. Centen.

ANNALI DI MERCEOLOGIA SICILIANA. Vol. I. 1932–1933. Istituto di Merceologia: Catania, 1934.

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THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

An Ordinary Meeting of the Society was held at the Chemical Society's Rooms, Burlington House, on Wednesday, May 2nd, the President, Mr. John Evans, F.I.C., being in the chair.

Certificates were read in favour of John Ferguson Brown, B.Sc., A.I.C., Carl Emil Resch, B.Sc., Wilfred Smith, B.Sc., A.I.C., and Sidney George Edward Stevens, B.Sc., A.I.C.

The following were elected members of the Society:—Frederick Frank Beach, M.A., B.Sc., F.I.C., Thomas Gifford Elliot, F.I.C., Frederick John Flowerdew, B.Sc., A.I.C., M.P.S., John Arthur Heald, M.C., B.Sc., F.I.C., Francis Edwin Needs, F.I.C., and Derrick John Saxby, B.Sc., A.I.C.

The following papers were read and discussed:—"The Determination of Free Silica in Coal Measure Rocks," by A. Shaw, B.Sc.; "A New Apparatus for Determining the Temperature of Crystallisation of Cocoa Butter," by S. A. Ashmore, B.Sc., A.I.C.; "The Determination of Small Quantities of Germanium in the Presence of Arsenic," by S. A. Coase, B.Sc.; and "The Saturated Fatty Acids of Chrysalis Oil," by S. Ueno and H. Ikuta.

Obituary

WILLIAM ELLAND WOOLCOTT

By the death of William Elland Woolcott, on April 14th, the Society has lost one who will be much missed, especially by his fellow consultants.

Mr. Woolcott was a partner in the firm of A. Norman Tate & Co., with whom he had been associated for forty-six years, practically all his adult life, and was well known for his work on oils and fats. He served on the Committee appointed by the Ministry of Food, under the Chairmanship of the late Otto Hehner, to report on Standard Methods of Analysis of Seeds, Nuts and Kernels, Fats and Oils and Fatty Residues, which completed its labours in 1919 (see Analyst, 1920, **45**, 278).

He joined our Society in 1921, and was elected a Fellow of the Institute of Chemistry in 1922. Of a singularly modest and retiring disposition, he was seldom heard at meetings of the chemical societies which he attended, but his confrères knew him as one who was ever ready to assist them with his knowledge and advice on any subject of which he was a master.

A few years ago a serious illness affected his health, but he continued working in the laboratory until some days before his death at the age of 65. His nervous temperament caused him, of late years, to worry over the future welfare of his colleagues and assistants, and the time of business depression left its mark upon him. There is little doubt that this incessant anxiety weakened his powers of resistance, and thereby hastened his end.

The funeral, which took place at Bebington Cemetery, was attended by Mr. W. Roscoe Hardwick and the writer.

F. ROBERTSON DODD

The Determination of Small Quantities of Fluorides in Water

BY GUY BARR, B.A., D.SC., AND A. L. THOROGOOD, B.SC.

(*Read at the Meeting, April* 4, 1934)

WE have made a short study of the application of the zirconium-alizarin reagent of de Boer (*Rec. Trav. Chim. Pays-Bas*, 1925, **44**, 1071; *Chem. Weekbl.*, 1924, **21**, 404) to the colorimetric determination of small quantities of fluorides. After the work had been completed a paper by Elvove (*U.S. Public Health Reports*, 1933, **48**, 1219) appeared, describing a procedure nearly identical with that which we had evolved; many of the observations given below are, however, not to be found in his brief note. References to the literature of the subject will be found in Elvove's paper.

The stock solutions used in making the reagent were: (*a*) 3·53 grms. of zirconium oxychloride ($ZrOCl_2.8H_2O$) dissolved in 100 ml. of distilled water (1 ml. contained 10 mgrms. of zirconium); (*b*) 1 grm. of sodium alizarin monosulphonate dissolved in 100 ml. of water and filtered.

To determine the optimum proportions in which solutions (*a*) and (*b*) should be mixed, a series of mixtures was made containing a fixed volume of (*b*) and differing volumes of (*a*). It was found that when the volume of (*a*) was less than one-fourth that of (*b*) the solution was dark yellow; with higher proportions of (*a*) the reagent was of a reddish-violet colour. On standing for 24 hours a reddish precipitate was formed in the mixed solutions unless the proportion of (*a*) to (*b*) exceeded 1·2 to 1. As a reagent for determining traces of fluorine in water, 3 ml. of (*a*) were mixed with 1 ml. of (*b*) and diluted to 200 ml. with distilled water. One ml. of this reagent gave with 50 ml. of water a faint pink colour, which was discharged by small quantities of fluorides.

Since de Boer stated that the sensitivity of the fluoride reaction was increased by the addition of hydrochloric acid, experiments were made to determine the optimum concentration of acid. Additions of more than 5 per cent. of concentrated (10*N*) hydrochloric acid to the test-water in the presence of the diluted reagent reduced the colour considerably, even in the absence of fluoride. Reduction of the amount below 5 per cent. made the fluoride reaction very slow.

It was not possible to include the desired amount of hydrochloric acid in the reagent by diluting the mixture of (*a*) and (*b*) with acid instead of with water, since this mixture gave a reddish precipitate on standing for 24 hours. In the absence of acid the diluted reagent remained clear for at least a month.

Thompson and Taylor (ANALYST, 1933, **58**, Abst., 369) and Casares and Casares (*Anal. Fís. Quim.*, 1930, **28**, 1159; *Chem. Abstr.*, 1931, **25**, 550) used an acid of approximately 2·5 per cent. concentration. Thompson and Taylor increased the speed of reaction by heating, whilst Elvove, who used approximately the same acid concentration as we have done, allowed the test-waters to stand overnight before matching. By using the procedure outlined below it was found possible to secure accurate matching after the solutions had stood for ten minutes only.

To test the sensitivity at low fluoride concentrations, six sodium fluoride solutions were prepared so as to contain from 0 to 1 part of fluorine per million in distilled water. Fifty ml. of each solution were transferred to a Nessler cylinder, 2·5 ml. of concentrated hydrochloric acid (10 *N*) and 1 ml. of the reagent were added, and the mixture was allowed to stand for ten minutes. It was possible to arrange the cylinders in the order of their fluorine-content, the colour varying from pink with no fluorine to brownish-yellow with one part of fluorine per million.

In estimating the fluorine-content of a sample of water it was necessary to ascertain the order of the concentration before proceeding to a precise determination.

This was done by matching the test-sample, by the procedure described above, against a series of standards containing, say, 1, 2, 4, 6 and 8 parts of fluorine per million. If the colour of the test-sample faded at a rate between that of standards 4 and 6, a further series was prepared, sub-dividing the range between these two standards; the process was continued until a perfect match was obtained. For concentrations higher than 2 parts per million the pink colour obtained with 2 ml. of reagent changed to yellow with an inconvenient rapidity. It was necessary, therefore, in the definitive comparison, to use a larger volume, such that a very faint tinge of pink remained in the sample and in one of the standards after ten minutes; thus, for a fluorine-content of 5 parts per million, the volume of reagent was increased to 2 ml. It was found possible to determine the fluorine-content of a sample of potable water containing 5 parts of fluorine per million with an accuracy of 0·1 part per million. Such an accuracy cannot be obtained by Elvove's method, which is essentially similar to that used by us for the preliminary examination, although he suggests, in a footnote, that the proportion of reagent should be adjusted in the manner which we have found to be essential for rapidity and precision.

Concentrations of potassium, sodium and magnesium, exceeding those occurring in potable waters, were not found to affect the fluorine estimation. Since indications were obtained that the presence of unusual proportions of calcium, iron and sulphates interferes with the determination, it may be necessary, in some cases, to make the final colour comparisons with synthetic solutions having a composition similar to that of the water under examination. Thompson and Taylor have shown that, in determining the fluoride concentration in sea water, considerable discrepancies may arise unless the comparisons are made with waters of equal chlorine-content.

SUMMARY OF METHOD.—To 50 ml. of the water, contained in a Nessler glass, add 2·5 ml. concentrated HCl; mix, and then add such a quantity of the following reagent that a very faint pink tinge remains after standing for 10 minutes. The reagent is made by mixing 3 ml. of a zirconium solution (3·53 grms. $ZnOCl_2$, $8H_2O$ per 100 ml. of water) with 1 ml. of a 1 per cent. solution of sodium alizarin monosulphonate in water, and diluting to 200 ml.; for fluorine-contents below 1 part per million, 2 ml. of the reagent give a sufficiently intense pink colour, whilst for 5 parts of fluorine per million 4 ml. will be required, and will yield an orange colour. The colour produced must be matched against that given by standards containing known concentrations of fluorine (as sodium fluoride) treated similarly and at the same time. When the order of concentration is unknown, it is convenient to make a preliminary estimate from the *rate* of disappearance of the pink colour, using 4 ml. of reagent with standards containing 1, 2, 4, and 8 parts of fluorine per million.

This investigation was undertaken, at the request of Mr. N. J. Ainsworth, to obtain a method suitable for the routine examination of drinking waters in connection with studies on dental defects due to fluorides. The cost has been defrayed by him, and we desire to thank him for permission to publish the details.

THE NATIONAL PHYSICAL LABORATORY
TEDDINGTON, MIDDLESEX

The Clinical Significance of Traces of Fluorides in Water

BY N. J. AINSWORTH, M.C., M.R.C.S., L.R.C.P.

(*Read at the Meeting, April* 4, 1934)

IT has been recognised for some years that excess of fluorides in the diet of animals will produce changes in metabolism which manifest themselves in various parts of the organism.

This pathological condition is termed "fluorosis," and the organs chiefly affected are the bones. Schultz and Lamb,[6] in 1925, were the first to report on experimental fluorosis. It had not, at that date, been recognised as occurring naturally.

McCollum and his co-workers,[5] later in the same year, published an account of more extensive experiments on albino rats fed on a diet containing 226 parts of sodium fluoride per million. The changes reported affected not only the quality but also the growth of the bones, which, in general, seemed under-developed and of a more porous nature. The teeth were dull and opaque, and the normal yellow pigmentation of the front of the incisors was absent. The upper incisors also were so altered in shape that they failed to meet and to be ground away by the lower incisors; they consequently, grew in a circle until they penetrated the skull.

It was not for several years that the condition of the teeth of animals so fed was associated with the endemic disease or dystrophy called by Dr. Black,[1] in 1915, "mottled teeth" from their patchy white appearance; it was left to two chemists, Petrey and Churchill[7], in 1930, to demonstrate that the water supply in all affected areas in U.S.A. contained over two parts per million of fluorine, and the connection between this fact and the mottling was proved experimentally in the following year by Smith and Lantz[4], working independently.

A far severer condition is found in North Africa—termed by the French workers "le Darmous." In this the bones and general health, as well as the teeth, are affected, and the condition is sometimes fatal. These cases, I believe, occur in areas where the water flows over certain phosphatic strata—these natural phosphates are contaminated with fluorides.

Velu[8] carried out experiments on rats, to whose diet were added 1½ to 3 parts per cent. (40 to 80 parts per million of fluorine) of natural phosphate (Moroccan and Algerian phosphates).

The results were much more severe than those recorded by McCollum, and included various forms of paralysis, delayed growth, suppression of the sex cycle, death of offspring, goitre, atrophy of the bone marrow and loss of appetite, as well as the usual alterations in the teeth.

Velu produced similar symptoms by feeding rats on calcium fluoride which, I understand, is almost insoluble, whereas McCollum and most other workers used soluble salts, such as sodium fluoride.

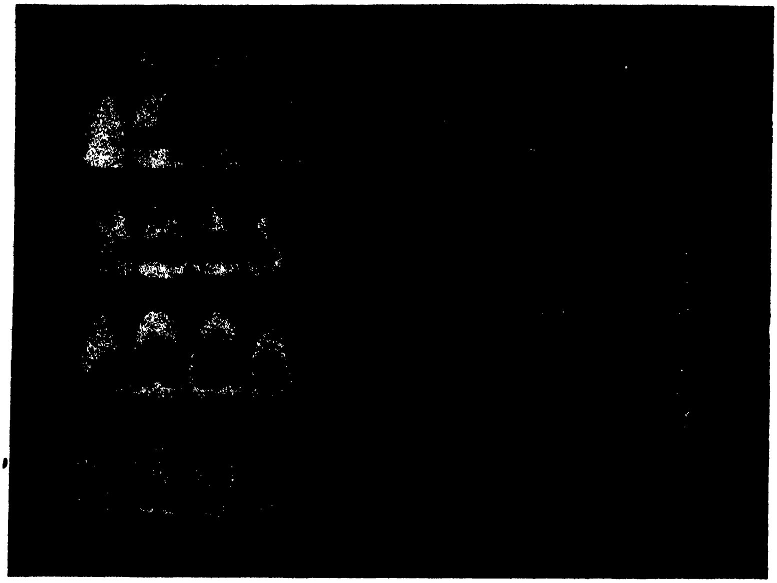
So much for the damage produced by abnormal amounts of fluorides in the diet. There is one other point of some interest. Is fluorine, which is found in all bones, particularly teeth, an indispensible element in the diet?

Last year, McCollum and Sharpless[9] carried out feeding experiments to answer this question, and found that no disadvantage was suffered by rats whose diet contained practically no fluorine; teeth and bones were normal, growth and reproduction unaffected. The interesting point is that in these animals no fluorine could be detected in the teeth.

It, therefore, appears that fluorine, either in food or in the body, is a mere contamination, and is not necessary to life or health, but that small amounts are tolerated, whilst large amounts are definitely harmful.

My interest in this question of the fluorine contamination of water is mainly clinical. I first noticed the dental condition known as "mottled teeth," when a student, in a young patient from Maldon, Essex. Later I had the opportunity of examining a large number of Maldon school children, when it became clear that the condition was identical with that described by Black and Mackay,[1] in 1916, as occurring in many districts of the United States of America between the Mississippi and the Rockies, notably in Arizona (*cf.* Dean[3]). After the discovery, in 1930, that the water-supply of these districts contained fluorine, I re-investigated the Maldon conditions, and obtained various samples of the local drinking waters, together with additional photographs[3].

The analyses made by Dr. Barr by the procedure he has described showed that the water of unaffected areas was free from fluorine, whereas that from the affected areas contained between 4·5 and 5·5 parts per million.



Teeth of 8 children affected with fluorosis.
Left-hand column: ages 13-14. Right-hand column: ages 12 to 13.
[Reproduced from a drawing, by permission of *The British Dental Journal* (1933, **55**, 233).]

A very high proportion (about 90 per cent.) of the children born and bred in these areas were affected, the essential condition being that they should be drinking the water during the years when the teeth were being formed. Once the teeth were through the gums the condition could not be influenced one way or another.

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DISCUSSION

The **PRESIDENT** said that he was sure all were grateful to the authors for bringing such important papers before them. He asked what was the normal amount of fluorides they had found in ordinary drinking waters, and what variations had been recorded.

Dr. G. **MONIER-WILLIAMS** said that the authors of the papers were to be congratulated on this piece of work. This was the first time that the connection between fluorine and mottled teeth had been established in this country. It provided one more instance of the great effect on metabolism which might be exerted by minute amounts of certain substances. The effect of fluorine on bone formation had been known for many years. In Maercker's book on the manufacture of alcohol reference was made to the feeding of cattle on distillery residues containing fluorides used as yeast antiseptics. The bones of the cattle were found to be seriously affected.

This matter was of great interest to analysts, in view of the fact that fluorides were seriously advocated some time ago as preservatives. Preparations containing fluorides were openly sold as butter preservatives, and it was claimed that sodium silicofluoride was absolutely non-toxic. Fluorides might also occur in phosphate baking powders and flour improvers made from rock phosphate. Obviously, the presence of more than the merest traces of fluorine was highly undesirable.

Another point of interest was the proposal that silicofluorides should be used as insecticides in agriculture. In France, barium silicofluoride was used against the Colorado beetle, and it was suggested that it should be used on potato crops in this country. If confined to the potato haulm, it might not be objectionable, but the case would be different if it were used on the edible parts of crops.

It was curious that there should be fluorine in the Maldon water. One would have expected it to occur in parts of Derbyshire, but not in water from the London clay. What was the mode of action of fluorine on teeth? Did it remove calcium or did it interfere in any other way with calcium-phosphorus metabolism? Statements in the literature as to the fluorine-content of bones and of sound and unsound teeth were very contradictory.

Mr. D. M. **FREELAND**, referring to Dr. Monier-Williams' remark regarding insecticides, said that a short time ago he was asked to examine an insecticide, and it contained roughly 50 per cent. of *Dalmatian* flowers and 50 per cent. of sodium fluoride. The manufacturers stated that it would not harm animals. He could understand that they would not wish to eat it, but if it were to get on to any food it would certainly have bad effects. Undoubtedly sodium fluoride should not be put about indiscriminately in houses or factories.

Mr. F. W. F. **ARNAUD** said that he had known of the use of sodium fluoride in fly poisons for many years. He asked if fluorine had been determined in ordinary drinking water apart from that in the Maldon area?

Mr. A. L. **BACHARACH** suggested that, in a district where the water contained fluorine, all the produce in the locality might be similarly contaminated, so that the mottled teeth and other pathological conditions might not be due solely to the fluorine in the water. An examination of the fluorine-content of the produce grown and consumed in the district might be desirable to elucidate this matter. It was perhaps vain to speculate at this stage, but one could not help wondering if the ingested fluorine "locked up" some of the available calcium, much as beryllium presumably locked up phosphorus in experimental "beryllium rickets."

Mr. C. E. **SAGE** asked whether any of the effects described had been noticed among workers using hydrofluoric acid. He had never come across such mottled teeth among men using the acid. Maldon was one of the few places where salt was produced from sea-water. Was the effect on teeth peculiar to Maldon because of the use of such salt, or, had it been noticed where the salt was prepared from brine pumped in Cheshire or Worcestershire? He also asked if the method was applicable to food.

Mr. W. J. A. BUTTERFIELD remarked, apropos of the Maldon water, that he believed it was a fact that most of the water supplies in Essex contained a comparatively large proportion of chlorine. Was the chlorine in Maldon water in anything like the same ratio to the fluorine as it was in sea-water? He asked this because chlorine extended in relatively high proportions to chalk water from deep artesian wells in Central London. One found these wells, which were sunk by owners of big blocks, to contain organically unimpeachable chalk water, with 16 to 20 parts per 100,000 of chlorine. This was undoubtedly due to very slow infiltration of sea-water from the bed of the river, where the sea-water lay almost undisturbed by the ebb and flow of the tide. Fresh water passed down and sea-water passed up the river, but on the bed there was very little change with the tidal conditions, and he thought it possible that the chlorine-content of the waters in Essex was due to that slow infiltration of sea-water from the coast and tidal rivers.

Dr. J. GRANT asked if the authors had tried the bleaching effects of fluorides on the colour produced by titanium salts and hydrogen peroxide. He had used this method with larger quantities of fluorine, and for water it would only be necessary to concentrate the fluorine by evaporation. He believed the salt industry in Essex was very old, and it would be of interest to know if mottled teeth had been noticed before the last 100 years or whether they were comparatively recent.

Mr. E. HINKS asked whether all forms of fluoride would act in the same way in this test. If there were silicofluoride, would that react in the same way as a simple fluoride?

Dr. H. E. COX asked whether any effect on the bones or other constituent parts of the body had been noticed at the *post-mortem* examination of persons with mottled teeth.

Dr. BARR, replying, said that they had determined the fluorine in only five samples of Maldon waters; these had been furnished by Mr. Ainsworth, and were found to contain from about 1 to 5 parts of fluorine per million. According to the analyses supplied, the content of sodium chloride was of the order of 50 grains per gallon, so that the maximum ratio of fluorine to chlorine was nearly $1{\cdot}2 \times 10^{-2}$. The average ratio F/Cl reported by Thompson and Taylor (*loc. cit.*) for samples taken in the open sea, at depths of from 0 to 2500 metres, was only $7{\cdot}0 \times 10^{-5}$, and they remarked that much higher ratios were found in inland waters. As the ratio for the Maldon water was 170 times as great as that for sea-water, it was not likely that the fluorine-content was due to infiltration from the sea. Thompson and Taylor gave a list of substances which definitely did not interfere with the determination when present in amounts likely to occur in sea-water; these included iron, carbonates, sulphates, bromides, and iodides. It was probable that a suitable technique could be devised to make the method applicable to food-stuffs. The authors had not tried the process with silicofluorides; according to Robertson, Marriott and Humphreys (*J. Soc. Chem. Ind.*, 1934, **54**, 83T) the reaction mixture should be warmed to 70° C., and allowed to cool before comparison of the colours if silico-fluorides were present.

Mr. AINSWORTH, replying, said that the condition of mottled teeth occurred mainly in Arizona. It was found in a few scattered districts in North and South Dakota and Tennessee, but it was practically unknown in the Eastern States of America. He had no knowledge of the effect of traces of fluorine on the body, but the bones of rats which had been given a high proportion of fluorine looked white and patchy. With regard to the point raised by Mr. Sage, mottling of teeth was produced only in teeth in course of formation. All the photographs shown were those of children; in the particular school which these children attended, the teeth of 80 per cent. of the children were mottled. Adults who came into the district were not affected.

The Analysis of Green Teas

By THOMAS McLACHLAN, F.I.C., and MARGARET IDA STERN, B.Sc., F.I.C.

Owing to a dispute concerning the ash of a sample of gunpowder tea a short time ago we had occasion to search the literature for figures and found that, while many are published for black teas, few are available for the green variety. Having a collection of samples in the laboratory, we thought that it might be of service to examine these and place the results on record. In doing this we have not used new methods; in fact, in our opinion, one of the disadvantages of many published figures is the use of new methods by authors. It may, however, be well to state briefly the methods we have employed:—

Moisture.—Two grms. of the semi-powdered tea were dried in a flat weighing bottle in an electric oven at 100° C. for 1 hour, cooled and weighed. The sample was re-heated for half-hour periods until constant in weight.

Ash.—One grm. was ashed in a platinum capsule at as low a temperature as possible over a Bunsen or Argand burner. The ash was extracted with 30 ml. of boiling water, the extract was filtered through a small filter, and the residue was washed with boiling water until about 100 ml. of filtrate had been collected. The filtrate was cooled rapidly and titrated with $N/10$ hydrochloric acid, first with phenolphthalein and then with methyl orange as indicator. The ash insoluble in water was treated with 15 ml. of boiling dilute (1 : 1) hydrochloric acid to obtain the acid-insoluble portion. The residue was treated with hydrofluoric and sulphuric acids to separate silica.

Water Extract.—The water extract was determined by the method of Tatlock and Thomson (Analyst, 1910, **35**, 103).

Tannin.—This was estimated by the Löwenthal-Procter method (Leach, *Food Inspection and Analysis*, 4th Ed., p. 383).

Caffeine.—Caffeine was determined by the Bailey-Andrew method (*Official and Tentative Methods of the Assoc. Offic. Agric. Chem.*, 3rd Ed., p. 155).

Unfortunately, there was insufficient material available to enable us to complete the analysis of every sample. Sow Mee is a broken tea, rather better than dust; the other varieties require no explanation.

A suggestion was made that the high ash figures might be due to "facing" with talc, and considerable attention has therefore been given to this question. According to the literature, the amount of talc employed for this purpose seldom exceeds 1 per cent., whereas the amount of matter insoluble in hydrochloric acid is considerably above this figure in most of our samples. It was noticed that every sample of gunpowder tea, except Nos. 6 and 7, appeared to have been

	Gunpowder														
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Sample	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Moisture, per cent. ..	9·03	9·14	8.89	8·56	9·83	7·96	7·62	8·55	7·99	8·35	8·43	8·04	9·56	9·25	8·61
Extract, per cent. ..	53·1	51·7	50·3	48·4	54·3	56·6	55·6	52·9	56·3	48·8	48·8	54·3	51·7	53·1	54·2
Total ash, per cent. ..	8·1	8·1	9·1	9·2	8·0	6·1	5·60	8·6	8·0	8·49	9·70	9·96	10·16	10·3	5·5
HCl required for neutralisation of water-soluble ash from 1 grm. (phenolphthalein), ml. *N*/10 ..	0·95	0·45	0·6	0·6	0·7	0·7	1·05	0·25	0·64	0·60	0·95	0·70	0·85	0·9	0·6
HCl required for neutralisation of water-soluble ash from 1 grm. (methyl orange), ml. *N*/10	3·3	2·75	2·9	2·5	3·0	3·1	3·50	1·7	2·7	3·15	3·15	2·15	3·25	2·85	2·8
Ash soluble in water, per cent.	4·3	3·6	2·4	2·3	3·8	4·0	3·75	3·1	3·7	3·74	3·35	3·39	3·05	2·55	3·6
Ash insoluble in water, per cent.	3·8	4·5	6·7	6·9	4·2	2·1	1·85	5·5	4·3	4·75	6·35	6·57	7·11	7·75	1·9
Ash insoluble in water, soluble in 50 per cent. HCl, per cent. ..	2·6	2·8	4·3	3·2	2·3	1·8	1·6	2·8	2·3	3·01	3·27	3·42	3·38	4·50	1·52
Ash insoluble in HCl, per cent.	1·2	1·7	2·4	3·7	1·9	0·3	0·25	2·7	2·0	1·74	3·08	3·15	3·73	3·25	0·38
Ash insoluble in HCl, less silica, per cent. ..	0·4	0·4	0·5	1·0	0·3	0·2	0·10	0·8	0·5	0·56	0·93	1·11	1·3	1·95	0·1
Silica, per cent. ..	0·8	1·3	1·9	2·7	1·6	0·1	0·15	1·9	1·5	1·18	2·15	2·04	2·43	1·3	0·28
Tannin, per cent. ..	10·52	7·69	6·90	9·37	8·59	9·70	10·58	12·40	13·35	12·49	7·37	9·91	7·86	9·00	—
Caffeine, per cent. ..	2·10	2·17	—	2·20	2·27	3·37	3·23	2·08	2·73	1·98	—	2·67	2·17	2·20	—

	Sow Mee											Japanese green			Suey		Kee-mum	Oo-lono
	1	2	3	4	5	6	7	8	9	10	11	1	2	3	1	2		
Sample	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33
Moisture, per cent. ..	8·34	9·23	9·39	9·45	8·91	8·54	8·64	9·08	8·69	8·84	8·17	7·56	6·92	6·42	9·46	9·83	9·95	8·99
Extract, per cent. ..	52·3	49·4	48·5	48·3	53·3	52·3	48·1	50·5	49·7	49·6	48·3	52·5	45·4	53·4	46·3	45·5	52·0	54·3
Total ash, per cent. ..	7·6	9·05	9·06	8·94	8·2	5·93	7·62	9·52	7·95	10·85	8·45	6·87	8·9	7·9	6·37	5·93	5·75	6·57
HCl required for neutralisation of water-soluble ash from 1 grm. (phenolphthalein), ml. $N/10$ ..	1·3	0·70	0·60	0·70	0·65	0·80	0·45	0·50	1·1	0·4	0·65	0·8	1·4	1·6	0·55	0·95	1·1	0·65
HCl required for neutralisation of water-soluble ash from 1 grm. (methyl orange), ml. $N/10$	3·5	2·15	2·65	2·35	3·25	3·35	2·75	2·85	3·7	1·9	3·15	3·65	3·1	3·3	3·25	3·25	3·65	3·15
Ash soluble in water, per cent.	3·7	2·60	3·27	3·48	3·29	3·33	3·04	3·48	3·65	3·35	3·35	3·8	3·3	3·2	3·57	2·5	3·95	3·35
Ash insoluble in water, per cent.	3·9	6·45	5·79	5·46	4·91	2·60	4·58	6·04	4·3	7·5	5·1	3·07	5·6	4·7	2·8	3·43	1·8	3·22
Ash insoluble in water, soluble in 50 per cent. HCl, per cent. ..	2·8	4·48	3·88	3·61	2·95	2·25	3·30	3·22	2·3	4·1	2·8	1·85	3·0	2·95	2·4	2·93	1·35	2·20
Ash insoluble in HCl, per cent.	1·1	1·97	1·91	1·85	1·96	0·35	1·28	2·82	2·0	3·4	2·3	1·22	2·6	1·85	0·40	0·50	0·45	1·02
Ash insoluble in HCl, less silica, per cent. ..	0·4	0·46	0·60	0·60	0·90	0·15	0·43	0·92	0·8	1·2	0·8	0·37	1·0	0·75	0·15	0·1	0·17	0·3
Silica, per cent. ..	0·7	1·51	1·31	1·25	1·06	0·2	0·85	1·90	1·2	2·2	1·5	0·85	1·6	1·1	0·25	0·4	0·28	0·72
Tannin, per cent. ..	9·54	6·48	6·30	—	9·00	9·0	7·74	8·56	6·84	5·70	7·2	8·77	8·37	9·60	5·77	3·98	7·34	11·04
Caffeine, per cent. ..	—	2·03	1·83	—	2·20	2·03	2·2	—	2·17	—	1·77	2·73	2·18	2·52	2·58	2·3	3·83	2·42

"faced" with talc, but it was found impossible to remove this by shaking with water, as suggested in the literature. When attempts were made to remove the talc, it was found that other mineral matter was removed at the same time. The ash insoluble in hydrochloric acid from every sample was examined microscopically and gave the impression at first that, in all but one or two samples, talc was present. This seemed unreasonable, since talc would be expensive as a loading material and could not account for the high amount of matter insoluble in water, but soluble in hydrochloric acid. The particles of siliceous matter insoluble in hydrochloric acid were extracted from a piece of the Great Wall of China in our possession and, when examined microscopically, showed a structure almost identical with that present in most of our samples. The silica from very fine sand was very similar, as were also the silicates insoluble in hydrochloric acid from Cornish china clay and fuller's earth, but that present in powdered pumice (passing a 180-mesh sieve) was considerably more angular.

It is, therefore, concluded that there is no apparent reason to think that the ash of green tea need really be much greater than that of black tea, although there does not appear to be any method of checking it at the moment. At the same time, it is our opinion that the high ash is due, in the main, to extraneous dirt, rather than to actual "facing."

In view of the suggestion in the paper of Tatlock and Thomson (ANALYST, *loc. cit.*), that China teas contain an excess of caffeine, as against the high tannin-content of black teas, it is interesting to note that our results do not enable us to draw any such inference.

Micro-Volumetric Determination of Sulphur and Chlorine in Organic Compounds with the Use of an Assay Balance

BY DOUGLAS W. COWIE AND DAVID T. GIBSON

THE simple micro-volumetric method described by Pregl (*Quantitative Organische Mikroanalyse*, 3rd Ed., p. 163) for determining sulphur in compounds free from nitrogen and halogen can be extended to the determination of sulphur and halogen by absorbing the combustion gases in standard alkali. The total acidity is determined, the solution concentrated, and the halide content determined by Volhard's method.

Unfortunately, we were limited to the use of an assay balance reading to 0·01 mgrm., but the following table (which gives a series of 36 unselected analyses) shows that the method is capable of results within the usually accepted limits. The analysis takes 3 to 4 hours and requires 4 to 6 mgrms. of substance.

Working from right to left the apparatus, as far as V, is the same as recommended by Pregl for the determination of sulphur, except that certain simple modifications greatly increase its reliability.

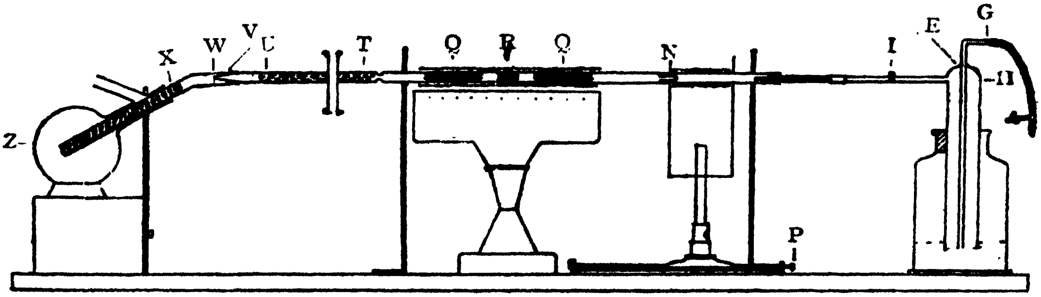
(i) E is a glass seal, thus ensuring the relative levels of the inner (G) and outer (H) tubes. Pregl's cork joint is liable to slip gradually. The tube (H) has a lip, like a beaker, to facilitate the escape of any excess pressure.

(ii) The substance is contained in a hard glass tube (N) (not a boat); combustion is more even and danger of flashing is minimised.

(iii) Between the platinum contacts Q, Q′ a short piece of silica, R, wound round with platinum wire ensures a more thorough mixing of the gases.

(iv) We find it a great advantage to terminate the filling so as to leave an empty space, UV. The capillary end, V, is otherwise liable to be sealed by a drop of liquid. Since introducing this feature we have never been troubled with this.

(v) The movable Bunsen burner is much more evenly advanced if it is mounted on a screw, P.



Such an apparatus retains sulphurous gases completely when the glass spirals, T, are moistened with water; but halogens, as Pregl found, can be retained only by alkali. As it was impracticable to moisten the glass spirals with an exact amount of alkali, we have added the guard tube, WX, which, together with the flask, Z, is moistened with 5 ml. of N/50 sodium carbonate solution. The guard tube fits over the main combustion tube, and the joint is made gas-tight with a drop of water.

The combustion is carried out exactly as described by Pregl (3·5 ml. oxygen per minute being a convenient speed).

TABLE I

(CHLORINE IN SULPHUR-FREE COMPOUNDS)

Substance	Chlorine found, per cent.		
	Alkali	Silver nitrate	Theory
Chloro-camphor ..	19·0	19·0	19·0
	19·1	19·0	
p-Dichlorobenzene ..	48·0	47·8	48·3
	47·8	48·0	
	47·8	47·9	

When the combustion is completed, tap I is closed and the guard tube disconnected. This tube is washed clean with 20 ml. of distilled water from a wash-bottle with a very fine jet. The main combustion tube is then washed out with a further 15 ml. of distilled water, and one drop of perhydrol is added to the combined washings in the flask, which is allowed to stand for ten minutes. Perhydrol not only oxidises any sulphite, but reduces oxy-acids of chlorine to chloride (Viebock, *Ber.*, 1932, 586). The solution is then boiled vigorously for two minutes and cooled, one drop (= 0·03 ml.) of a mixed methylene blue and methyl red indicator is added, and the solution is titrated with *N*/100 sulphuric acid until the green colour disappears. The solution is again heated to boiling, and cooled, and more standard acid is added until the colour swings from an intense green to a definite violet with one drop of acid. It is necessary to boil the liquid, as the indicator is affected by the presence of carbonic acid, but the actual end-point is much sharper in a cold solution.

TABLE II

(SULPHUR AND CHLORINE)

Substance	Chlorine, per cent.		Sulphur, per cent.	
	Found	Theory	Found	Theory
Ethyl-α-chlorocamphor-10-sulphonate	12·1 12·0	12·1	10·6 10·6	10·9
$Cl_2C_6H_3SO_2SC_6H_3Cl_2$	36·3 36·5	36·6	16·1 16·1	16·5
$ClC_6H_4SO_2SC_6H_4Cl$	21·6 22·2 22·2	22·3	19·6 20·0 19·9	20·1
$ClC_6H_4SO_2CH_2COCH_3$	15·4 15·3	15·3	13·7 13·8	13·8
$(ClC_6H_4)_2SO_2$	24·2 24·7	24·7	11·2 10·9	11·2
*$(C_2H_5SO_2)_2CCl_2$	23·9	26·4	24·0	23·8
$ClC_6H_4SO_2CH_2COCH_3$	15·3	15·3	13·6	13·8
$(ClC_6H_4)_2SO_2$	24·7	24·7	11·0	11·2
$(C_2H_5SO_2)_2CCl_2$	26·6 26·5	26·4	23·9 24·1	23·8
$ClC_6H_4SO_2CH_3$	19·0	18·6	16·9	16·8
$ClC_6H_4SO_2CH_2COCH_3$	15·0 15·0	15·3	13·9 13·8	13·8
$Cl_2C_6H_3S.SC_6H_3Cl_2$	39·6 39·6	39·9	18·0 17·8	18·0
$(ClC_6H_4)_2SO_2$	24·9 24·9	24·7	11·4 11·3	11·2
$ClC_6H_4SO_2CH_3$	19·0 18·9	18·6	17·0 17·0	16·8
$\left.\begin{matrix}(C_2H_5SO_2)_2\\(C_6H_5SO_2)\end{matrix}\right>CCl$	9·7 9·5	9·5	25·6 25·6	25·6
$CH_3C_6H_4SO_2Cl$	18·6 18·8	18·6	17·1 17·1	16·8
$Cl_2C_6H_3SO_2Cl$	43·3 43·7	43·4	13·2 13·1	13·0
$CH_3C_6H_3(OCH_3)SO_2Cl$	16·2 16·2	16·1	14·3 14·6	14·5
$C_{10}H_7SO_2Cl$	16·0 15·9	15·7	14·1 14·0	14·1

* Compound subsequently found to be impure.

The solution, which is contained in a 100-ml. quartz distilling flask, is then heated on a water-bath while a stream of filtered air is drawn over the surface. In an hour 60 ml. are thus reduced to 10 ml. This concentrated solution is titrated with silver nitrate (1 ml. = 0·5 mgrm. of chlorine) until no further turbidity is observed, filtered and back-titrated with thiocyanate solution. If the solution is not concentrated, it is very difficult to observe the end-point; and if too much silver nitrate is used, the excess tends to be occluded, so that rather high results are obtained.

UNIVERSITY OF GLASGOW

The Determination of Zinc in large Quantity, with particular reference to the Analysis of Brass

BY L. C. NICKOLLS, M.SC., D.I.C., A.I.C., AND J. G. N. GASKIN, B.SC., F.I.C.

THE analysis of alloys containing high percentages of zinc is rendered difficult by the lack of methods suitable for determining this metal accurately in the quantity usually taken for analysis. For example, 2 grms. of brass contain 0·6 to 0·8 grm. of zinc, but for the accurate determination of this quantity there appears to be, at present, no convenient method, so that the zinc-content is frequently reported as a difference figure, or by a determination on a weighed aliquot part of the solution of the metal. Neither of these methods being entirely satisfactory, we have examined and tested the standard methods for the determination of zinc, with a view to adapting the most suitable to the determination of the total zinc-content of alloys such as brass.

PRELIMINARY EXPERIMENTS.—Three methods have been examined. In the preliminary experiments a 50-ml. portion of a sulphuric acid solution of 10 grms. of zinc in a litre was taken. Later experiments were made on weighed aliquot parts of a solution twice this strength.

Method I (Precipitation as zinc ammonium phosphate and ignition to pyrophosphate).—The conditions for quantitative precipitation are critical. The precipitate is easily filtered in a Gooch crucible and ignited, but the results are consistently high.

Zinc taken Grm.	Zinc found Grm.
0·5002 (volume)	0·5058
	0·5064
	0·5070
0·5002 (weight)	0·5021
	0·5044

Method II (Precipitation as zinc pyridine thiocyanate and ignition to oxide).—The precipitate obtained from 0·5 grm. of zinc was excessively bulky and difficult to handle. After prolonged ignition it contained varying proportions of carbon, zinc sulphide and zinc sulphate.

Zinc taken Grm.	Zinc found Grm.
0·5002 (volume)	0·5066
	0·5050
	0·5048
0·5002 (weight)	0·5046

Method III (Electrolysis of the zinc in alkaline solution).—Of the three methods, this is the simplest in operation, and the results obtained showed that it is the most accurate.

Zinc taken Grm.	Zinc found Grm.
0·5002 (volume)	0·5015
	0·5031
	0·5022
0·5002 (weight)	0·5008
	0·5010
	0·5007

Method III was accordingly selected as the most suitable for our purpose.

INVESTIGATION OF METHOD III.—It is well known that zinc is deposited on the cathode when an alkaline solution of this metal is electrolysed. Further, it is well known that nitrates and ammonium salts prevent this deposition. We have confirmed this; traces of nitrates hinder the deposition, and small quantities entirely prevent it. It is also recorded that at temperatures in excess of 20° C. the zinc is not deposited. We have found that, even if deposited at about this temperature, the zinc may easily re-dissolve as the solution becomes warmer. At low temperatures (0° C.) the deposit is firm and closely adherent. In our experiments, therefore, the vessel containing the electrolyte was immersed in an ice-bath. With a rotating gilt platinum cathode, and a current density of 0·035 amp. per sq. cm., 1 grm. of zinc was deposited in an hour and a half at this temperature.

In our first experiments the cathode, having been washed thoroughly with water, was dipped in alcohol and dried at 100° C. for 5 minutes. This gave high results, obviously, as appearance indicated, owing to surface oxidation.

	Per Cent.
Zinc found (alcohol drying)	36·77
	36·79
Zinc present (from analysis)	36·60

Later, acetone was substituted for the alcohol, and the cathode was dried in the steam-oven for less than a minute. The resultant deposit showed no signs of surface oxidation. When the electrolysis is properly carried out the whole of the zinc is deposited, and no traces are left in the solution.

APPLICATION OF METHOD III TO THE ANALYSIS OF BRASS.—To apply the electrolysis of zinc to the analysis of brass required some consideration of the salts likely to be present in the solution. From what has been said it is obvious that the removal of copper by electrolysis in nitric acid solution must be followed by some operation designed to remove the nitric acid. For this purpose tests were made with metallic aluminium. Reduction with aluminium carried out in a warm alkaline solution proved adequate to remove the nitric acid as ammonia, the last traces of which could then be removed by boiling. This, however, led to a further difficulty, inasmuch as at least 6 grms. of aluminium were necessary to remove the nitric acid in a normal analysis of brass, and this quantity of aluminium, particularly in the presence of tartaric acid, rendered it difficult to deposit the whole of the zinc, and, further, had a slightly adverse effect on the nature of the deposit.

This procedure was, therefore, abandoned in favour of an attempt to make a separate determination of the zinc in hydrochloric acid solution. Electrolysis of the zinc is unaffected by the presence of alkali chlorides. The brass was, therefore, dissolved in a mixture of hydrochloric acid and the minimum quantity of nitric acid, and the acids were removed by evaporation to dryness. It remained, then, to remove the copper in the solution obtained after the addition of water to the dry chlorides. It was found that aluminium, in the practically neutral solution, completely replaced the copper, leaving a coagulated precipitate, easily filtered. The best results were obtained when the replacement took place in a hot solution, which was continuously agitated to displace the precipitated metal from the surface of the aluminium. The solution being, moreover, nearly neutral, no copper was re-dissolved, and unnecessary quantities of aluminium in solution were avoided. If the replacement takes place in the cold, some cuprous salts are formed by reduction, and it is impossible subsequently to convert these salts into metallic copper. One grm. of aluminium was found to be more than sufficient to replace all the copper when 2 grms. of brass were used for the determination.

Tin and other possibly interfering elements are dealt with after the description of the method which follows:—

METHOD FOR THE DETERMINATION OF ZINC IN BRASS.—Two grms. of brass, in the form of fine drillings, are dissolved in a mixture of 10 ml. of water, 7 ml. of concentrated hydrochloric acid and 3 ml. of concentrated nitric acid. This solution is evaporated nearly to dryness, after which a little bromine is added and the evaporation is continued to dryness on the water-bath. The salts are dissolved in 50 ml. of hot water and 5 grms. of anhydrous sodium sulphate are added. To the hot solution are added two pieces of aluminium foil, each about 0·5 grm. in weight, and the replacement of the copper is allowed to proceed as rapidly as possible, the contents of the beaker being agitated with a rod throughout the operation. The solution is left in contact with the aluminium for one hour, after which it is cooled and filtered, and the precipitate is then well washed with cold water. Fresh 50 per cent. sodium hydroxide solution is added to the filtrate until the precipitates of zinc and aluminium are re-dissolved, and any small precipitate is then removed by filtration.* Otherwise a further quantity of sodium hydroxide is added to the solution to give an excess equivalent to 20 ml. of 50 per cent. caustic soda. This solution is electrolysed by means of a rotating gilt platinum cathode, the beaker containing the electrolyte being placed in an ice-bath. Electrolysis is carried on for an hour and a half, with a current density of 0·035 amp./cm^2, the electrodes being about 2 cm. apart; after this the whole of the zinc should have been deposited. The cathode is removed with the current still running, washed thoroughly with cold water, dipped in acetone and dried for half a minute in a steam-oven, cooled and weighed. The electrolyte should be examined for any traces of zinc by passing hydrogen sulphide through the liquid; but, if electrolysis has been correctly carried out, zinc should be absent.

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* Copper left in solution will appear at this stage as a yellow precipitate, and, since its removal is difficult, it is best, unless the quantity is quite small, to make a fresh determination.

EFFECT OF OTHER METALS AND THE MODIFICATION IN PRESENCE OF IRON.—When iron or manganese is present in quantities greater than 0·05 per cent., it is advisable to adopt a modified procedure after the removal of the copper, since some zinc is invariably co-precipitated by sodium hydroxide with the iron and manganese hydroxides.

The solution is oxidised with bromine, treated with sodium hydroxide as before, and heated to boiling, and the iron and manganese hydroxides are removed by filtration. These are dissolved in hydrochloric acid and re-precipitated with ammonia. After filtration, any zinc in the filtrate may be recovered by any of the standard methods, or, alternatively, an excess of sodium hydroxide is added, the ammonia removed by boiling, the solution returned to the main bulk, and all the zinc electrolysed in one operation.

The presence of small quantities of lead, tin, nickel or magnesium does not affect the accuracy of the method.

Tin is partly volatilised as stannic chloride during the first evaporation, but most of it is removed as insoluble metastannic acid during the filtration of the copper precipitate, the first evaporation having the twofold purpose of removing the nitric acid and fixing the tin. Similar remarks apply to the small quantities of arsenic commonly found in brass.

The addition of sodium sulphate, after the evaporation to dryness, precipitates most of the lead present, and this is, therefore, also removed during the filtration of the copper. Any traces remaining in solution are removed as carbonate by filtration of the alkaline solution.

It was observed that nickel behaved similarly to copper and was completely replaced by aluminium.

Magnesium is largely removed as oxychloride during the filtration of the copper, but traces remaining in solution are precipitated later as hydroxide and may be removed by filtration of the alkaline solution.

EXPERIMENTAL RESULTS.—The above method was successfully applied to a sample of brass having the following composition:—

	Per Cent.
Copper	61·67
Tin	1·29
Lead	0·41
Iron	nil
Arsenic	0·03
Zinc (by difference)	36·60
	100·00

The following percentage results were obtained for the zinc-content:—**36·65, 36·66, 36·54, 36·64 36·53.**

We have to thank Sir Robert Robertson, K.B.E., F.R.S., for permission to publish this paper.

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The Determination of Bismuth in Copper

By E. W. COLBECK, M.A., S. W. CRAVEN and W. MURRAY

Introduction.—In view of the uncertainty of many of the methods for the chemical separation of small amounts of bismuth from copper, a new method has been evolved depending on the formation of a bismuth mirror when copper millings are heated at 1050–1060° C. in a stream of hydrogen.

According to F. Paneth (*Ber.*, 1918, **51**, 1704), a gaseous bismuth hydride can be formed which is comparatively stable at ordinary temperatures, but is decomposed at high temperatures. F. Paneth and E. Winternitz (*loc. cit.*) obtained the hydride from a bismuth-magnesium alloy in sufficient quantities to permit of its detection by the formation of a mirror or by luminescence tests. If such a hydride could be obtained, it would afford a means of separation of bismuth from copper, since, according to the literature, the latter element does not form a hydride.

A separation need not necessarily depend upon the formation of a bismuth hydride, since it is possible that above a certain temperature bismuth might distil in an atmosphere of hydrogen, whilst no distillation would take place below this critical temperature. A paper published by T. G. Pearson, P. L. Robinson and E. M. Stoddart (*Proc. Roy. Soc.*, 1933, [A], **142**, 275) suggests that this alternative is more probable. In either case deposition of metallic bismuth should take place at some point in an enclosed system.

Experimental work showed that bismuth could be separated quantitatively from copper by heating in a stream of hydrogen. The following method embodies the conditions that have been found most satisfactory:

Apparatus.—The apparatus required is as follows:

A horizontal electrically-heated tube furnace, 24 in. long, capable of being maintained at 1060° and fitted with a thermo-couple for the measurement of the temperature of the middle of it.

A clear silica combustion tube 36 inches long, 7/8 in. internal diameter drawn out at one end to 1/4 in. diameter.

Fire-clay combustion boats, as used in the determination of carbon in steel.

A supply of hydrogen gas and a suitable flow-meter.

Procedure.—A portion of the sample of copper, in the form of fine turnings or millings, is weighed out into a fire-clay boat, which is then introduced into the centre of the coal-furnace. Hydrogen at the rate of about 18 litres per hour is passed over the sample; when all the air is expelled from the tube the escaping gas is ignited. The temperature of the furnace is then raised to 1060° C., and maintained there for 1 hour. At the end of this time the furnace current is switched off, the rubber at the end of the silica tube is detached, the hydrogen supply is cut off, and the bung at the entry end of the silica tube is removed. A small explosion occurs, after which the boat is extracted, and the silica tube is removed from the furnace and allowed to cool. The drawn-out exit end is then stoppered by means of a glass rod attached to it by rubber tubing, and the bismuth mirror is dissolved off with concentrated nitric acid. Very little acid is required for this purpose, and the amount used should always be so regulated that 100 ml. of the resulting solution does not contain more than 2 ml. of concentrated acid. The tube is washed out with distilled water, the solution is made up to a known volume, and an aliquot portion is taken, the bismuth content of which should not exceed 0·0004 grm.

This aliquot portion is placed in a Nessler cylinder, 6 drops of an aqueous solution of sulphur dioxide (1 vol. of a saturated solution with 3 vols. of water) and 5 ml. of a 2 per cent. aqueous solution of potassium iodide are added. The same volumes of these reagents and a volume of nitric acid equal to that present in the test solution are introduced into a second Nessler cylinder. The volumes in both cylinders are made up to 100 ml., and the standard bismuth solution, containing 0·0001 grm. of bismuth per 1 ml., is added to the second cylinder until the colours match.

After the determination, starch solution is added to both tubes to make sure that the colours are not caused by free iodine. If a blue colour is obtained, the determination should be repeated, a larger volume of sulphur dioxide solution than is specified above being used. The standard bismuth solution is made by dissolving bismuth metal in nitric acid.

When it is impossible to obtain fine millings (*e.g.* granulated copper), the temperature must be raised above the melting-point of the sample, *i.e.* to 1100–1120° C. After the expiration of one hour the furnace should be allowed to cool, the hydrogen stream being maintained until the temperature has fallen well below 1084° C. In this way spitting of copper is prevented.

EARLY EXPERIMENTAL WORK.—That bismuth can be separated from copper in a stream of hydrogen was shown in the following preliminary experiment:—An intimate mixture of a known weight of electrolytic copper and a known weight of finely-divided bismuth metal was made, placed in a boat, and heated in a stream of hydrogen at 1050° C. A mirror, readily soluble in nitric acid, was formed about 9 inches from the boat. A colorimetric determination of bismuth in this solution showed that this mirror contained the whole of the added bismuth. Bismuth added, 0·0142; found, 0·0145 per cent.

This experiment was repeated on a known weight of pure bismuth oxide instead of bismuth metal, with the following result:—Bismuth oxide added, 0·0076 grm.; found, 0·0077 grm. (determined as Bi). The hydrogen used in the above experiment was taken straight from a gas cylinder to the furnace. Two similar determinations were carried out in which hydrogen, dried by passing through calcium chloride and phosphorus pentoxide drying tubes, was used. Quantitative separation of the bismuth was again effected in both cases.

Samples of copper containing bismuth were treated in a similar manner; in every instance a deposit similar to that described above was obtained in the same place on the tube.

ESTABLISHMENT OF THE METHOD.—To show that the method was quantitative, the following procedure was adopted. Sufficient copper millings to make a small ingot were treated for the removal of bismuth by the mirror method. The residues left in the boat were allowed to cool to room temperature in a stream of hydrogen to prevent oxidation, and were afterwards melted in a H.F. induction furnace. A representative sample was taken from the ingot for analysis. The remaining portion was weighed and re-melted and a known weight of bismuth metal was added. The bismuth melted readily without any signs of loss, such as fuming, and the melt was super-heated just sufficiently to allow it to be tapped. Since the high-frequency currents induced in the molten copper have a most pronounced stirring effect, a homogeneous ingot is obtained. There was no loss in weight during melting. A representative sample for analysis was taken from the second ingot. Analytical results are given in Table I:

TABLE I

Ingot	Addition made	Bismuth found by mirror method Per Cent.
Re-melted residues	None	Less than 0·0002
Re-melted residues plus a known weight of bismuth (metal)	0·0106 per cent. of bismuth as the metal	0·0105

For purposes of comparison these two samples were analysed for bismuth by the method depending upon the co-precipitation of bismuth carbonate with calcium carbonate. The results are given in Table II:

TABLE II

Ingot	Additions made	Bismuth found by co-precipitation method Per Cent.
Re-melted residues	None	Trace
Re-melted residues plus a known weight of bismuth (metal)	0·0106 per cent. of bismuth as the metal	0·0075 per cent.

Two samples of electrolytic copper, supplied by I.C.I. (Metals), Ltd., were examined by the mirror method, and found to contain 0·0015 per cent. and 0·0020 per cent. of bismuth, respectively. These amounts of bismuth are much higher than the maximum allowed for this type of copper under British Standard Specification No. 198 (1925). The two electrolytic copper samples were also analysed by the co-precipitation method, and were found to contain 0·00016 per cent. and 0·00015 per cent. of bismuth. In view of this high figure for bismuth in electrolytic copper as determined by the mirror method, it is of interest to note that a sample of vacuum-melted copper was tested by this method and found to contain 0·001 per cent. of bismuth.

In further tests on the mirror method as compared with the method depending on the co-precipitation with calcium carbonate, a series of copper ingots was prepared. Electrolytic copper was used as a base metal, and known weights of bismuth metal were added to it. The results are shown in Table III:

TABLE III

		Mirror method		Co-precipitation method	
Ingot number	Bismuth added Per Cent.	Bismuth, theoretical Per Cent.	Bismuth found Per Cent.	Bismuth, theoretical Per Cent.	Bismuth found Per Cent.
Electrolytic copper (base)	—	—	0·0015 0·0016	—	0·00015 0·00015
S.1	0·00483	0·0064	0·0058 0·0058	0·0050	0·0043 0·0047 0·0046
S.2	0·00953	0·0111	0·0098 0·0100	0·0097	0·0083 0·0084 0·0087
S.3	0·0483	0·0499	0·0500 0·0495	0·0485	0·043 0·046
S.4	0·0968	0·0984	0·098 0·098	0·097	0·086 0·086

In the above table the theoretical bismuth percentage is equal to the percentage of bismuth metal added plus the percentage of bismuth found by the method in question.

It will be observed that in all four cases the mirror figures are much closer to the theoretical values than those of the co-precipitation method. In S.1 and S.2 the difference in the percentage of bismuth present in the electrolytic copper, as determined by the two methods, has a considerable influence on the theoretical percentage of bismuth. In S.3 and S.4, however, where the added amounts of bismuth metal are much higher, the figure for the base metal does not influence the theoretical percentage very much. Yet in both S.3 and S.4 the co-precipitation method gives results that are still 10 per cent. below the theoretical amount.

CONSIDERATION OF THE EFFECT OF POSSIBLE IMPURITIES.—Of the impurities likely to be present in copper, arsenic and antimony, owing to the readiness with which they form hydrides, are the elements likely to interfere with the determination of bismuth by the mirror method. To investigate the possibility of such interference, samples having a known percentage of bismuth and containing also arsenic and antimony were analysed. The results are given in Table IV:

TABLE IV

Sample mark	Bismuth theoretical Per Cent.	Additions	Bismuth found by the mirror method Per Cent.
S.8	0·0175	None	0·0170
S.7	0·0174	0·001 per cent. of antimony	0·0170 0·0170 0·0168
S.11	0·0213	0·018 per cent. of arsenic	0·0199

Apparently, therefore, neither arsenic nor antimony has any serious effect on the accuracy of the results obtained by the mirror method.

Our thanks are due to the Directors of Imperial Chemical Industries, Limited, for permission to publish this work, which was carried out in the Research Department of their subsidiary company—I.C.I. (Alkali), Ltd., Northwich.

Notes

The Editor wishes to point out that the pages of the Journal are open for the inclusion of short notes dealing with analytical practice and kindred matters. Such notes are submitted to the Publication Committee in the usual manner.

THIOCYANOGEN VALUES OF SOME EGYPTIAN SESAME AND COTTON-SEED OILS

The thiocyanogen values of some Egyptian vegetable oils were determined by the method described by Kaufmann (ANALYST, 1926, **51**, 157; 1928, **53**, 613).

The results, and the proportion of esters of saturated acids calculated from the formula

Esters of saturated acids = 100 − 1·16 × thiocyanogen value

are given below.

SESAME OIL

Thiocyanogen value	74·5	74·4	76·1	74·3	74·4	75·5	74·5	74·8	74·6	74·9	75·5
Esters of satd. acids	13·6	13·7	11·7	13·8	13·7	12·4	13·6	13·2	13·5	13·1	12·4

COTTON-SEED OIL

Thiocyanogen value	63·2	64·8	64·3	63·4
Esters of saturated acids	26·7	24·8	25·4	26·5

It should be noted that the reagent does not keep for more than three days; low results are obtained after this period. When 50 ml. of the reagent and 0·1–0·12 grm. of oil are used, the amount of thiocyanogen absorbed is equivalent to 5 or 6 ml. *N*/10. As the margin of error is about 0·05 ml. *N*/10 thiocyanogen in the titration, this error is of the order of 1 in 120 in the result.

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LABORATORIES
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THE DETERMINATION OF ARSENIC IN TARTAR EMETIC

A MODIFICATION of the German Pharmacopoeia method for the detection of arsenic in tartar emetic can be made quantitative by colorimetric comparison with standards. Two grms. of the sample are weighed into a colourless test-tube, of about 15 mm. diameter, and 5 ml. of arsenic-free hydrochloric acid are run in. One ml. of stannous chloride reagent (B.P.) is then added, and the solution is heated just to the boiling-point to dissolve the tartar emetic. The tube is then allowed to stand, and the colour which develops is compared, by reflected light, against a sheet of white paper, with standards containing 2 grms. of pure arsenic-free tartar emetic and standard arsenic solution equivalent to 0, 0·015, 0·02, 0·025 mgrms., etc., of arsenic treated in precisely the same way. Certain substances, such as traces of mercuric chloride, accelerate the reduction considerably, and addition to the acid solution of 1 or 2 drops of a 0·01 per cent. solution of mercuric chloride causes separation of the arsenic quickly enough for a comparison of colour to be made after about 15 minutes.

Any potassium chloride that separates can be re-dissolved by adding a few drops of water, or the original hydrochloric acid may be diluted with 10 per cent. of water.

The accuracy of the method is within about 2 parts per million when the arsenic present is not appreciably in excess of the limit of the B.P.; when a large number of samples have to be examined the method is a simple and extremely rapid sorting test.

It is worth noting that samples of tartar emetic belonging to the same consignment contained widely varying proportions of arsenic, the amounts ranging between less than 5 and more than 60 parts per million.

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NOTE ON THE DIPHENYLAMINE TEST FOR NITRATES IN MILK AND ITS RELIABILITY IN THE PRESENCE OF SMALL QUANTITIES OF CHLORINE

IT is, of course, as Elvidge points out in his note in THE ANALYST (1934, 170), well known that this test is not specific for nitrates, but is given by other oxidising agents. The large number of routine tests which we have made, giving no evidence of traces of nitrates or other oxidising agents, however, indicates that interference by these oxidising agents very rarely occurs in practice. Hypochlorite is the oxidising agent most likely to be encountered, but, on theoretical grounds, it appeared to us to be very unlikely that such a reactive substance would persist unaltered in milk in high dilution and give the diphenylamine reaction. We considered it desirable, therefore, to ascertain the limits to which hypochlorite can be detected, (i) in aqueous solution, and (ii) in milk, by the diphenylamine test, and at the same time to establish controls with nitrates under exactly the same conditions. The following results were obtained:

In water

0·1 part per 10^6 of nitrogen, as nitrate (but not less) is detected with certainty
5·0 parts „ „ chlorine (but not less) are detected with certainty

In milk

0·25 part „ „ nitrogen as nitrates (but not less) is detected with certainty
100 parts „ „ chlorine (but not less) are detected with certainty

In milk, 400 times as much chlorine as nitrogen (as nitrates) is required to give the blue colour.

We are, therefore, quite unable to agree with the statement of Elvidge, that 0·1 part per million of chlorine, or anything like so small a quantity, in milk can be detected, and, in our opinion, it is extremely improbable that the diphenylamine test for nitrates in milk will be affected by hypochlorites conveyed to the milk from milking machines, separators, etc., to which it has been applied for cleaning purposes.

In the application of these tests, Lerrigo's technique (ANALYST, 1930, **55**, 433) has been adhered to, the time given for the development of colour being not more than half an hour.

It is well known that the presence of the chloride ion is necessary for the detection of very small amounts of nitrates by means of the diphenylamine test; in its presence the test is about ten times as sensitive. In the detection of chlorine the sensitiveness is independent of the presence of the chloride ion; this suggests that the reaction is not the same.

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NITRATES IN MILK

OVER forty years ago, the late Mr. H. Droop Richmond published his opinion that cows drinking nitrated water produced milk that gave the diphenylamine test for nitrates (ANALYST, 1893, **18**, 279; 1894, **19**, 83). Since that time his opinions have been quoted upon many occasions (in depreciation of the value of the detection of nitrates in milk), and most recently by Elvidge (ANALYST, **1934**, 170).

In my note ("The Routine Detection of Nitrates in Milk," ANALYST, 1930, **55**, 430) I stated that the above opinions were based on faulty manipulation of the test. This statement not only represented my conviction based upon experience, but had the authority of Mr. Richmond himself behind it. I had been in communication with him on the matter, and, in view of the repeated quoting of his early opinions, I have been asked to publish part of the letter which he wrote to me in October, 1929. It reads as follows:—" . . . I may say, however, that at the present time I am by no means convinced that there was not some pitfall in the observation which I made then. The method I was using was to float the milk on a sulphuric solution of diphenylamine, and I can distinctly remember that in the case where I was under the impression that I found nitrate, there was a very slight blue colour produced. I am not, however, now convinced that this blue colour was necessarily due to the presence of nitrates. . . . I think I may say that if I had known as much about the diphenylamine reaction in those days as I do now, I should have been chary in reporting the presence of nitrates."

A. F. LERRIGO

LABORATORY OF THE CITY ANALYST
BIRMINGHAM

NOTE ON NITRATES IN MILK

A PAPER by Elvidge (ANALYST, 1934, **59**, 170) refers to the practice of sterilising dairy utensils with hypochlorite solutions, and gives a series of results obtained in the detection of such solutions in milk.

The author states that he was able to detect one part per million of chlorine with ease, and that one in ten millions was just discernible with the diphenylamine test (Lerrigo, ANALYST, 1930, **55**, 433). Diphenylbenzidine (Monier-Williams, ANALYST, 1931, 56, 397) gave a tenfold increase in delicacy, from which it is to be assumed that one part of chlorine in one hundred millions was just discernible.

I have attempted to obtain similar results, but have met with complete failure except with high concentrations. The disinfectant "Milton" was used as a source of hypochlorite and was standardised by arsenite in the usual way.

Quantities of chlorine varying from one in one thousand to one in ten millions were used, and the diphenylbenzidine test was employed in all cases. Positive results were obtained only with concentrations of one in a thousand and one in ten thousand, but the former concentration is so high as to be detectable by its odour, and it renders the milk undrinkable.

Elvidge further states that a concentration of one part of chlorine in ten millions gives a colour about equal in depth to that given by one in ten millions of nitrate. Attempts to repeat this resulted in a very deep blue with the nitrate, but a negative result with the chlorine.

The ortho-tolidine test gave negative results in all cases. Attempts to apply the starch-iodide method of detection similarly proved of no value. With this, a concentration of one in one thousand of chlorine gives an intense blue—as was to be expected, since free chlorine can be detected by its odour. One part in ten thousand liberated iodine, but did not colour the starch blue, giving instead a yellowish colour due, no doubt, to the iodo-protein complex. All other concentrations gave negative results.

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BUFFERS FOR THE LACTIC FERMENTATION

WHEN pasteurised separated milk is soured with a good starter of lactic streptococci (including aroma bacteria) lactose is fermented, mainly to lactic acid, and the citric acid (average 0·16 per cent.) almost disappears (about 0·03 per cent. is left), yielding volatile acids, the molecular weight of which corresponds with acetic acid (average 0·08 per cent.). The total acidity, volatile acidity and aroma of the culture can often be increased by adding a little citrate to the milk.

If we compare the acidities of milk, diluted milk, and whey, both before and after fermentation, such results as these are obtained:

	Skim milk	75 per cent. skim	50 per cent. skim	25 per cent. skim	Whey
Original acidity.. ..	0·18	0·13	0·08	0·04	0·11
Final acidity	0·92	0·74	0·49	0·27	0·39
Acidity of fermentation	0·74	0·61	0·41	0·23	0·28

The acidity is titrated with $N/10$ alkali (phenolphthalein as indicator), and calculated as lactic acid. In each case only a fraction of the lactose is fermented. The differences in the acidities of fermentation are due mainly to the amount of buffers in the solutions. What is measured is the amount of lactic acidity which the bacteria can produce before the hydrogen ion concentration of the medium is increased from, say, p_H 6·6 to p_H 4·2, though there are minor complications.

If the buffer action of a substance has to be measured, 1 part of skim milk may be diluted with 3 parts of a neutral solution of the buffer, and its fermentation compared with that of a control diluted with water, each having received an addition of 2 per cent. of sour milk starter.

In this way neutral citrates, acetates and phosphates are found, as can be predicted, to increase the final acidities, and so they are buffers. Casein, albumen, peptone, and gelatin have buffer action, which is limited with the last mentioned (by solubility). Commercial pepsin, pancreatin and rennet extract are likewise buffers. By the action of pepsin on casein or albumen the buffer action of these can be made to equal, then exceed, that of Witte's peptone. Digestions with pancreatin reach a stage where the buffer action is diminishing. Lysine and asparagine gave negative results.

The addition of lactic acid before fermentation decreases the final acidities:

Lactic acid added, per cent.	0·00	0·04	0·08	0·13	0·17
Final acidity, per cent.	0·28	0·30	0·27	0·25	0·22

During a milk shortage reconstituted milk may be used for the fermentation, but this seldom ferments quite so well, and the addition of a little tri-sodium phosphate when dissolving the milk powder has been found useful.

The deposit which adheres to the pasteuriser (flash process) is rich in buffer substances, as the following figures (on the dry substance) show:

	I per cent.	II per cent.
Phosphoric acid (P_2O_5) ..	33·2	20·0
Protein	7·6	44·8
Citric acid	1·0	—

Acid production and growth are closely correlated with lactic bacteria; hence the importance of buffers.

D. W. STEUART

THE LABORATORY
GAYMER & SON LTD.
ATTLEBOROUGH

SILICOSIS AND ITS INCIDENCE IN THE GOLD MINES

THE statement (ANALYST, 1934, 191) that the dust from the gold-bearing quartz rock of the Kolar Gold Fields, India, has not produced any cases of silicosis is not borne out by the facts. A committee was appointed in 1931 to investigate this question, and the conclusion was reached that silicosis does occur in these gold fields. Moreover, Dr. L. G. Irvine and Dr. S. W. Simpson, who were consulted, reported that "the pathological and radiographic evidence appeared to create a *prima-facie* case that instances of silicosis do occur among the underground workers in the Kolar Gold Mines," and many cases of the disease have been definitely diagnosed by pathologists.

It is said that silicosis does not develop in the Kolar Gold Fields until after 10 to 15 years' work underground. This may be due to the fact that the quartz reef in these Gold Fields contains only 8 to 17 per cent. of free silica, as compared with 80 to 90 per cent. in the South African rock. It is possible that acicular aggregates of sericite may be found in the matrix of the Kolar quartz pebbles, though this point has not yet been investigated.

Y. V. S. IYER

PUBLIC HEALTH INSTITUTE
BANGALORE (CITY)
INDIA

Official Appointment

THE Minister of Health has approved the following appointment:—

HUGH AMPHLETT WILLIAMS as a Public Analyst for the Metropolitan Borough of Shoreditch, in addition to H. G. Harrison (May 3rd, 1934).

Notes from the Reports of Public Analysts

The Editor would be glad to receive the Annual or other Reports of Public Analysts containing matter of special interest to the Society. Notes made from such Reports would be submitted to the Publication Committee.

JERSEY

REPORT OF THE STATES' ANALYST FOR THE YEAR 1933

THE total number of samples examined was 4381, as compared with 4017 in 1932, and 337 in 1884 (when the first Official Analyst to the States of Jersey was appointed). Of these, 3032 were samples of soils, fertilisers, etc., 434 were spirits, tobaccos, etc., for the Finance Committee, and 477 were foods, drugs and waters for the Sanitary Committee.

SOIL-TESTING AND ADVISORY SERVICE.—Jersey soil yields two crops per year. The soil-testing service guides the farmer as to the fertilisers he should use. Generally, special fertilisers are prescribed, based on the simple tests for reaction, a judgment of physical condition, the past history of the soil, and the requirements of the proposed crops. The rapid increase in the number of samples of soil submitted (from 135 in 1925 to 3008 in 1933) proves that the service has justified itself.

SPRAYS.—Eleven samples of commercial sprays were examined; they contained from 12·2 to 30·5 per cent. of copper. For the determination of the copper-content the volumetric iodide method of the A.O.A.C. is used. Also, both dry sprays and preparations for wet sprays are shaken with a large volume of water and allowed to stand; the presence of free copper in solution has been found to be connected with "scorching," and the greater the amount of acid required to produce soluble copper the slower appears to be the action of the spray.

OILS AND IMPORT DUTIES.—A sample of olive oil was found to be genuine, and a "salad oil" contained not less than 70 per cent. of arachis oil, which is dutiable when it is a Continental, not an Empire product.

JERSEY MILK AND BUTTER.—The 93 samples of milk examined contained an average of 4·94 per cent. of fat and 9·44 per cent. of solids-not-fat. No prosecutions were instituted, certain poor samples being found to be the result of incorrect treatment of the cow.

Thirty-eight samples of Jersey butter were of good quality. Monthly samples taken from two of the best-known local dairies showed an average Reichert–Meissl value of 29·8 (32·3 to 28·2), and an average Polenske value of 4·0 (4·9 to 3·2).

The importation of cows, heifers and bulls into Jersey has been prohibited since 1789 (except that for a few years foreign cattle were imported for meat and killed on the quay). This purity of strain is almost certainly unique in the civilised world, and the Jersey breed has been exported in very large numbers. The figures show the quality of milk and butter they produce in their native island.

CREAM.—Thirteen samples of fresh liquid Jersey cream contained from 65·8 to 45·1 per cent. of fat (average 53·6 per cent.).

CANNED LIQUID EGG.—A sample had been preserved by rendering it slightly acid, the user being instructed to neutralise the acid with sodium bicarbonate when the egg was required for use in cooking.

WATER SUPPLY.—Of 210 samples of well- and rain-water examined, 100 were satisfactorily free from pollution, but 16 of these were contaminated with lead. The Jersey waterworks supply is obtained from surface streams; there are three reservoirs of 90 million gallons capacity in all, sufficient for fifteen weeks of the peak summer demand. In addition to the slow sand-bed filters, two types of mechanical pressure filters have been installed. The temporary hardness (as chalk) averages 1 part per 100,000, and coagulation of the aluminium sulphate is assisted by chalk or sodium aluminate, or both. Chloramine treatment has been used on the filtered water since 1930.

Tests for Traces of Chloroform.—A small bottle received from the police was empty, except for a little "dew" on one side. The bottle was suspected to have contained chloroform, and, on opening it, there was a strong smell of that drug. One ml. of alcohol was introduced into the bottle and shaken; on the resulting alcoholic solution reactions for chloroform were obtained by the carbylamine and Fujiwara's pyridine tests; chlorine was obtained on hydrolysis; and by Moffitt's modification of the Lustgarten test (Analyst, 1933, **58**, 2) 0·5 ml. of the alcoholic solution was found to contain 0·002 ml. of chloroform.

Urine.—A sample of "tea" from a workman's can contained 1·5 per cent. of urea and 0·5 per cent. of chlorine (with uric acid, calcium oxalate crystals and granular casts), corresponding with approximately 50 per cent. of urine.

C. P. Money

COUNTY OF KENT

Report of the County Analyst for the Fourth Quarter, 1933

Losses in Meat during Cooking.—Four pieces of meat were placed in the same oven and cooked for fifty minutes, after which the gravy and fat produced from each piece of meat were poured off and collected separately. The percentage losses in fat, gravy, etc., from the four steaks were as follows:

Home-killed	15·9	Argentine frozen ..	33·0
New Zealand frozen ..	27·9	Argentine chilled ..	31·2

The loss of weight on cooking English-killed beef was, therefore, only one-half of that sustained by the others. The loss of weight with all the colonial meats was very considerable, and amounted to about one-third of the total weight of meat. The importance of these losses lies in the fact that they determine the size and weight of the meat placed before a consumer after cooking. Whereas the loss sustained on cooking 16 oz. of English meat amounted to about 2½ oz., the loss with frozen meat was about 5 oz. The loss on cooking was not due to the frozen meat containing large quantities of fat, because the home-killed meat contained more fat than two of the other meats examined.

The gravy and fat were collected from each piece of meat after cooking and the amounts of these are below expressed as percentages of the fresh meat:

	Home-killed	New Zealand frozen	Argentine frozen	Argentine chilled
Fat	0·4	6·7	5·0	1·8
Gravy	5·4	11·5	16·7	16·3

The composition of the gravies was in every instance similar. Owing, however, to the large volume of gravy lost from the frozen meats, the total loss of nutrient matter was much greater than from English meat. The loss of soluble mineral salts from frozen and chilled meat is very considerable, amounting to as much as 31 per cent., whereas for English meat the loss is only about 12 per cent. The results now obtained confirm others which I have obtained, and clearly indicate that less cooked meat is obtained from frozen and chilled beef than from English-killed beef. The loss on cooking includes not only water and fat, but also certain quantities of soluble protein and, possibly more important still, water-soluble mineral salts. These losses are very much less with home-killed beef.

F. W. F. Arnaud

Legal Notes

Under this heading will be published notes on cases in which points of special legal or chemical interest arise. The Editor would be glad to receive particulars of such cases.

MIDDLINGS AND THE WHEAT ACT

R. AND W. PAUL, LTD. *v.* WHEAT COMMISSION

ON May 9th Mr. Justice Roche gave judgment in the action brought by Messrs. R. and W. Paul, Ltd., against the Wheat Commission, to obtain a decision whether, under the Wheat Act, 1932, wheat offals, known in the trade as "middlings," could be imported without liability to quota payment.

On various dates between April, 1933, and January, 1934, the plaintiffs had imported consignments of wheat offals, described as middlings, and, in particular, on October 24th, 1933, had received a parcel of middlings from Germany, and had paid an import duty on that parcel. Subsequently the Wheat Commission claimed quota payment on that parcel, but the plaintiffs contended that middlings were not liable to quota payments and refused to pay.

The Wheat Commission wished to have the question of the plaintiffs' liability settled by arbitration under a by-law, No. 20, of the Wheat By-Laws, 1932, made in pursuance of Sec. 5(1) and Sec. 5(2) (*m*) of the Wheat Act, 1932, but the plaintiffs contended that the by-law was invalid, and that they were not bound to submit to arbitration under by-law 20 on the question whether this consignment was liable to quota payment or was flour for the purposes of the Wheat Act, 1932. The plaintiffs also claimed the return of money which they had been obliged to pay in respect of other consignments of middlings from Germany.

The defendants contended that the by-law was valid, and that the Court had no jurisdiction to deal with the action. According to the definition in the Wheat Act, wheat offals are the residual products which, in the process of milling wheat, are extracted therefrom as germ or for animal or poultry food, and the defendants contended that nothing could be offal if it contained more than a normal quantity of material that could be extracted. With regard to the earlier consignments the defendants pleaded the Public Authorities Protection Act, alleging that the action had not been begun in time.

Sir Leslie Scott, K.C., and Mr. John Whyatt appeared for the plaintiffs; Sir William Jowitt, K.C., and Mr. Hubert Hull for the defendants.

Mr. Justice Roche decided that the Court had jurisdiction in the matter. The effect of by-law No. 20 of the Wheat By-laws, 1932, made in pursuance of sec. 5 of the Wheat Act, 1932, was, if valid, to obstruct all reference to the Courts. Mere authority to make by-laws at large was not authority to make by-laws of that nature. The Wheat Act did not authorise any such by-law as that.

His Lordship, in giving judgment, said that the real issue in the action was the construction of the statute. The parcels in question were said by the defendants to be the result of milling that was not in accordance with normal practice; therefore, it was said, that they were not offals and residuals within the definition of the Act, and therefore were flour.

The plaintiffs' contention was that those middlings were offals made as residual or by-products in the milling of flour; that they were substances extracted for animal or poultry food, and that they were therefore substances separated in the milling as wheat offals, and as such were expressly taken out of the category of flour, and did not attract quota payment. It was also said that, in so far as this might be material, fine or rich middlings, such as these, were produced before and at the time when the Wheat Act came into force, and were residuals or offals, and were known and described as such.

He found on the facts that all the parcels were separated in the milling of the wheat for flour as the primary product, and that they were separated in the milling as wheat offals or residual products.

With regard to the construction of the statute, it was his opinion that if the substances were, in fact, offals or residuals, and were intended for animal or poultry food, they were exempt from quota payment. No definition of flour or reference of the separation of offals to a standard was to be found expressed in the Act, and to give effect to the Commission's contention would be to legislate and not to interpret. An effort had been made to base a difference on the fact that fine middlings might be separated and used as flour. He found that that contention failed. The real point was that the millers, in the process of milling, had separated the middlings in question as a residuary product. On these facts he found that the plaintiffs were entitled to succeed.

With regard to the first three parcels, he held that the defence of the Public Authorities Protection Act was good, and covered those items of the plaintiffs' claim.

Judgment was given for the plaintiffs for £1912 5s. 2d., with a declaration of non-liability for payment where such payments had not yet been made. Leave to appeal was granted.

Report of the Departmental Committee on the Composition and Description of Food

THE Committee re-appointed by the Minister of Health and the Secretary of State for Scotland, on July 24th, 1933, have issued their Report, dated March 20th, 1934.* The terms of reference were as follows:

"To consider whether it is desirable that the law relating to the composition and description of articles of food should be altered so as to enable definitions or standards to be prescribed, or declarations of composition to be required, for articles of food other than liquid milk; and, if so, to recommend what alterations of the law are required."

The meetings were not open to the public, but opportunity was given to representative organisations to appoint persons to attend meetings when evidence was being taken, and memoranda were also received from the associations and other organisations set out in Appendix I of the Report. A list of the witnesses who gave evidence before the Committee is given in Appendix II. The minutes of the evidence are not printed in the Report, but it is suggested that copies thereof should be available for inspection at the offices of the Minister of Health and the Department of Health for Scotland. The Report deals with the questions submitted, under the following headings:

I. EFFECT OF EVIDENCE.—It is stated that virtually all the witnesses agreed that modern statutes and orders regulating the composition of food have operated in the public interest, and that their enforcement has proved practicable.

II. EXISTING DEFINITIONS, ETC.—It is pointed out that the Minister of Agriculture has power to make regulations respecting what is to be regarded as the normal composition of milk, cream, butter, and cheese. Reference is also made to the arrangement between the Society of Public Analysts and the Food Manufacturers' Federation as to the composition and labelling of specified descriptions of jams, to the voluntary grading of a number of articles by manufacturers who elect to use a prescribed "grade designation," and to definitions and standards in use in the Dominions and foreign countries.

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* Cmd. 4564. H.M. Stationery Office, Adastral House, Kingsway, W.C.2. 1934, pp. 18. April, 1934. Price 3d. net.

III. ADVANTAGES AND OBJECTIONS.—In the opinion of the Committee the effect of trade practice and competition on the character of certain articles indicates the desirability of having a power to fix definitions, but such power should be exercised in such a way as not to prevent reasonable development and improvement in the manufacture of an article. The objection that certain articles for which there is a demand might be driven off the market by the fixing of standards might be met by the sale of the sub-standard article under a name different from that of the standardised article.

The Committee have received no evidence that the lack of standards has resulted in malnutrition.

CONCLUSIONS AND RECOMMENDATIONS.

IV. THE MAIN QUESTION.—The Committee conclude that it is desirable that the law should be altered to enable definitions or standards to be prescribed or declarations of composition to be required, for articles of food other than liquid milk. The enabling power should be vested in the Minister of Health for England and in the Department of Health for Scotland (subsequently termed "the Minister" in the Report). In the opinion of the Committee, however, the case for the extension of standards or definitions to all articles of food has not been made out, although in some cases standards or definitions or declarations of composition are required for the protection of the consumers.

The Committee recommend that the power to fix standards should be used only where it is shown to be necessary for the protection of public health or the protection of the pocket of the consumer. Declarations of composition should be prescribed when it is desirable that the purchaser should be informed of some fact relating to either the composition or the preparation of the article. In any case, the power should only be exercised when the declaration can be checked by chemical analysis. The guiding consideration should be that, as far as possible, the same term should always mean the same thing.

Foods specially offered for infants and invalids should bear, on the label of the package containing them, a declaration of their contents.

Standards, declarations of composition, or definitions are not at present considered to be necessary for sweetmeats, unless it is found desirable to prohibit the use of certain ingredients.

It is suggested that the present limits or standards for arsenic, lead, tin, or other impurity, or for the addition to food of an ingredient claimed to be necessary (*e.g.* starch in shredded suet) should come under review.

V. ADVERTISEMENTS AND LABELS.—The Committee agree with the principle of the following recommendation, put forward by the Food Manufacturers' Federation, Patent and Proprietary Foods Section:—"It is our opinion that any attempt to control by statute statements about the composition of food will be stultified unless it is legally enacted that, for purposes of evidence as to the nature, quality and substance demanded of a food, specific claims made in advertisements shall be deemed to be part of the package label. Though it is theoretically true that the purchaser is expected to examine the label of a product before he completes its purchase, it is a matter of common knowledge that the vast majority of purchasers do not do so. The description on which they have been induced to buy the product is in a large number of cases only that contained in the advertisements, and we hold very strongly that progress in the standardisation and description of food will be seriously hampered until this matter is dealt with."

VI. WARRANTY.—The Committee consider that the retailer of a pre-packed article should be absolved from proceedings if he can show that he sold the article in the same condition as he received it, and had no reason to believe that it was not in accordance with legal requirements, and that he took all necessary precautions to protect it during storage.

The Committee also consider that the invoice referring to an article which may be the subject of a legal standard, and any label affixed to that article should be equivalent to a warranty that the article delivered may lawfully be sold under the name used.

Where samples of a pre-packed article on sale in the district of a Food and Drugs Authority are found to contravene legal requirements, action should be taken at premises where the article is packed.

VII. PROCEDURE FOR SETTLING STANDARDS AND DEFINITIONS.—The Committee do not recommend the constitution of a new permanent Advisory Committee, such as that advocated by the Society of Public Analysts and others. For articles in regard to which there should be no difficulty in arriving at a large measure of agreement with manufacturers and other interested parties the Minister, with the aid of his own experts, should consult any Government Departments concerned and confer informally with the manufacturers and others interested. Where there is a wide divergence of view between the parties interested it is recommended that the matter should be referred to a Committee of three independent persons who would hear evidence and report to the Minister. After receiving and considering the report it would be for the Minister to decide whether or not to proceed with the making of the Order.

Steps would have to be taken to prevent the importation of articles which contravened any standards or other requirements which had been laid down.

VIII. EXPENSES OF ADMINISTRATION.—The Committee are of opinion that alterations in the expenditure of Local Authorities resulting from the fixing of standards or definitions would not be material. They consider that the cost of administration would be materially reduced if the present law were amended by enacting that it shall not be essential to submit to chemical analysis an article of food, the nature or composition of which could be sufficiently proved in some other way.

IX. REVISION AND CONSOLIDATION OF STATUTE LAW.—It is generally agreed that the objects of the ancient statutes of pre-Victorian times dealing with the composition of tea and coffee are completely provided for by later legislation. The Committee therefore recommend that these Acts be repealed. Consideration should also be given to the question of replacing the two Acts of 1822 and 1836 (dealing with the composition of bread and flour) by new legislation more suited to present-day conditions. In the opinion of the Committee the time is ripe for the consolidation of the statutes dealing with the composition of food.

Report of the Committee on Trade Marks

THE Report of the Departmental Committee on the law and practice relating to trade marks was published on April 28th.*

The recommendations of the Committee include several that would involve fundamental changes in the existing law. Thus, it is recommended that a trade mark should be validly assignable for a part only of the goods for which it is registered, provided that such assignment is not likely to deceive or cause confusion.

Provisions should also be made for the registration, under proper safeguards, of persons authorised by a proprietor to use his registered trade mark. Provision should be made for the extended or defensive registration of a well-known registered trade mark, consisting of an invented word or words, which has become identified with the proprietor to such an extent that the use of the mark by others on goods other than those for which the mark is registered would create the impression that there was a connection between those goods and the proprietor of the mark.

A further recommendation is that the principle of the existing common law rule, whereby a word which is or has become the name by which an article is commonly known, is not protectable as a trade mark should be modified; and that Sec. 6(1) of the Trade Marks Act, 1919, should be amended so as to allow the proprietor of a word trade mark in respect of a patented article or substance to preserve his exclusive rights in the mark, if after a period of two years he can show that his trade mark is not the only practicable name or description of such article or substance.

The extension in certain directions of the legal rights of the proprietor of a validly registered trade mark is also recommended; in particular, the proprietor should be empowered to prohibit in relation to his trade mark certain acts which might injure the reputation or impair the value of his mark.

Definition of "Trade Mark."—The Committee propose that a "trade mark" other than a "certification trade mark" shall mean a mark used or proposed to be used by the proprietor upon or in physical or other relation to goods, for the purpose of indicating or so as to indicate a connection in the course of trade between the proprietor of the mark and the goods.

It is recommended that the operation of sec. 62 of the Trade Marks Act, 1905, should be limited to the registration in Part A of distinctive marks to non-trading bodies, and that such marks should, where practicable, be identified in use as certification marks. (*Cf.* ANALYST, 1933, **58**, 473.)

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* Cmd. 4568. H.M. Stationery Office, 1934. Price 1s. 6d.

Department of Scientific and Industrial Research

REPORT FOR THE YEAR 1932–33*

As in the previous year (ANALYST, 1933, **58**, 227), the Report is divided into five sections, comprising the Report of the Commission of the Privy Council for Scientific and Industrial Research (pp. 1–5); that of the Advisory Council (pp. 6–22); a Summary of Work (pp. 23–83); Research Associations (pp. 85–128); and 7 Appendices (pp. 130–179).

The Report of the Advisory Council deals at considerable length with the scheme started during the war to encourage the establishment by industry of research associations. The grant in aid of one million pounds voted by Parliament in 1917 is exhausted, and a general review of the position is made. The conclusion is reached that such research associations have proved their potentialities to an extent that warrants substantial development, and the urgent financial needs of the situation are emphasised. During the year under review the duty of directing and supervising the conduct of Road Research has been transferred to the Department, and a preliminary programme of research is being considered.

NATIONAL PHYSICAL LABORATORY.—The annual report of the Laboratory for the year has been published (ANALYST, 1933, **58**, 402). Since the Eighth General (International) Conference of Weights and Measures had various questions of international standardisation to discuss, the work of the National Physical Laboratory was brought to definite stages in anticipation. The results of the preliminary determination of the length of the metre in terms of the wave-length of the red radiation from cadmium have been published (J. E. Sears and H. Barrell, *Trans. Roy. Soc.*, 1932, A, **231**, 75), together with a description of the wave-length comparator, and the final determinations of the yard and the metre in air and *in vacuo*, in terms of light waves, and of the refractive index of air, have been completed and will be published shortly. A comparison of various sources of radiation for use with the comparator has also been made (J. E. Sears and H. Barrell, *Proc. Roy. Soc.*, 1933, A, **139**, 202). The results of the determination of the absolute unit of electric current by means of the ampere balance are now available, and it is found that the absolute ampere is greater than the international ampere by 12 parts in 100,000, the ratio being subject to a maximum uncertainty of 4 parts in 100,000. An inter-comparison of thermo-couples has been carried out by the Bureau of Standards, the Reichsanstalt and the National Physical Laboratory, and the scales have been brought into agreement within 0·1° C. at all points of the range 660° C. to 1063° C. Preliminary results on the use of a black-body radiator at the freezing-point of platinum as a primary standard of light show that agreement with the Bureau of Standards will be attained.

The Metrology Department have carried out the statutory decennial inter-comparisons of the Imperial and Parliamentary standards of length and weight. The comparison of the yard and metre standards is practically complete, and the new vacuum balance is being used for the comparison of the pound and kilogramme. The investigations on the thermal and electrical conductivities of heat-resistant alloys have shown that the thermal conductivities of the alloys examined tend towards a common value in the neighbourhood of 1000° C.

FUEL RESEARCH.—The Report for the year ending March, 1933, has been published (ANALYST, 1934, 34). Reference is made to the methods for the quantitative determination of coal ash (ANALYST, 1933, **58**, 614).

FOOD INVESTIGATION.—The Report for 1932 has been published (ANALYST, 1933, **58**, 611). Work on the metabolism of carbohydrates in fish has shown that in the haddock's liver glycogen decreases rapidly and disappears in 60 hours, whilst free sugar accumulates slowly and continues to do so after the complete disappearance of the glycogen; finally, after 150 hours, it reaches a maximum value corresponding with the loss of glycogen. A very small accumulation of lactic acid occurs over the whole period. The results of a detailed study of the quantitative variations in vitamin *A* of halibut liver oil are to be published. In addition to work already published on the metabolism of fat in fishes (*Biochem. J.*, 1932, **26**, 1978 and 1985), the fat of the salmon, as smolt, the porpoise, and, at the other end of the scale, the fats of certain members of the zöo-plankton, and of various algae are being investigated.

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* **Obtainable at Adastral House, Kingsway, W.C.2. Price 3s. net.**

The Ditton Laboratory is making a second series of experiments on the gas-storage of the following varieties of apples:—Monarch, Blenheim Orange, Worcester Pearmain, and Cox's Orange Pippin.

BUILDING RESEARCH.—Weathering measurements of atmospheric pollution are being tested in conjunction with Atmospheric Pollution Research Committee (ANALYST, 1934, 280). Progress has been made in the study of the physical factors influencing weathering, in the development of freezing and crystallisation tests and the correlation of their results with the behaviour of bricks, stone, etc., in structures, and with the exposure tests and stone preservative experiments. In the work on asphalts and bitumens good results have been attained with bitumen applied hot as an adhesive for bonding rubber flooring to concrete.

FOREST PRODUCTS RESEARCH.—The Report for the year has been published (ANALYST, 1933, **58**, 155). Work on the utilisation of thinnings from Forestry Commission and other plantations for telegraph and transmission poles has been in progress, particularly as regards their mechanical and physical properties and capability of absorbing creosote. The liability of timber to *Lyctus* infestation has been found to depend upon the relation between pore diameter and diameter of the ovipositor of the beetle.

METALLURGICAL RESEARCH.—Work on the removal of gases from light alloys has shown that there is on any exposed surface of molten aluminium an oxide skin which is highly impervious to gases, and to achieve the rapid elimination of gases the character of this skin must be altered. The nitrogen used to dilute the halide removes the liberated gas, and it is suggested that treatment with a mixture of raw cylinder nitrogen and carbon tetrachloride might be suitable in commercial practice. Further study of aluminium alloys capable of age hardening, and of the *X*-ray analysis of single crystals of high purity alloys is in hand.

WATER POLLUTION RESEARCH.—(See ANALYST, 1934, 282.)

CHEMICAL RESEARCH.—It is noted that some 38 British chemical firms and other outside organisations have applied to the Laboratory for advice and information. Two series of organic arsenicals have been investigated in the search for drugs to combat African sleeping sickness: derivatives of fluorenone and fluorenol containing arsenical groupings, and derivatives of *p*-arsanilic acid having the general formula $AsO_3H_2.C_6H_4.NH.CO(CH_2)_nCO.NRR'$.

ILLUMINATION RESEARCH.—The results of the investigation to discover the most suitable traffic signals have been embodied in a British standard specification. The investigation of the fundamental properties of diffusing glass-ware for the British Standards Institution has been continued.

RESEARCH ASSOCIATIONS

Only a few activities of a small number of these can be mentioned.

WOOL INDUSTRIES RESEARCH ASSOCIATION.—In both the woollen and worsted processes a method has been evolved whereby the fibres are treated in bulk to render them unshrinkable.

Ionised Oil for Wool Textiles.—A new type of oil known as ionised oil has been developed for wool textile purposes. This has been specially treated electrically, so as to be non-oxidisable, water-miscible, and to possess bleaching properties. The oil has now been in factory use for over a year, and thousands of yards of cloth, especially of the grey flannel type, have been processed with ionised oil, and put on the market.

Standardisation of Fastness of Fabrics.—The work carried on by the Society of Dyers and Colourists for the standardisation of fastness of dyed fabrics to various ordinary agencies has resulted in the selection of standard fabrics representative of 8 different degrees of fading, in red and in blue. Since wool dyestuffs usually are less susceptible to atmospheric fading, they have been used on a wool base. A series of standard tests expressing the degree of durability of standard fabrics has been drawn up.

LINEN INDUSTRY RESEARCH ASSOCIATION.—*Effect of Dyes on Tendering.*—It has been shown that when linen dyed with a range of vat and insoluble azo dyes is exposed in the open, excessive tendering occurs with a number of orange and yellow vat dyes. Some of the dyes examined, including several insoluble azo combinations, exert a protective effect under the same conditions.

The behaviour of cotton yarn dyed with a number of vat and insoluble azo dyes and woven as strips into linen glass cloths has been examined during a variety of laundry treatments. Some yellow and orange vat dyes have been shown to produce undue tendering when the material is exposed in the open between successive laundry treatments.

THE BRITISH FOOD MANUFACTURERS' RESEARCH ASSOCIATION.—*Research on Sterilisation.*—In the investigation of sterilisation problems of meat products, a report has been issued to members on the determination of the rate at which the heat used penetrates different types of products and sizes of packages. The temperature and time of heating required to destroy a particular type of bacterium which gave rise to serious trouble in several factories were investigated, and, although the spores were as resistant to heat as any so far recorded (standing boiling for over 7 hours, and surviving half an hour's heating to 230° F.), it was found not to be pathogenic, and its growth was inhibited by percentages of salt above a certain limit. Also, the older spores were found less resistant than the younger.

The reaction of certain types of bacteria to pickles of different strengths is being studied. One type will cause souring in bacon if the cure has been too mild, and the strength of salt that will inhibit growth is being sought. Results on the effect of salt on the growth of *B. coli communis* indicate that it is highly improbable that any of the bacteria usually associated with food poisoning outbreaks can survive the curing in a reasonably strong pickle.

D. G. H.

Addition to the Poisons Schedule

DINITRO PHENOL; DINITRO CRESOL

At a meeting of the Privy Council on April 11th the following resolution was received from the Council of the Pharmaceutical Society, acting in exercise of the powers vested in them by the Pharmacy Act, 1868, as amended by the Poisons and Pharmacy Act, 1908:

> "That by virtue and in exercise of the powers vested in the Council of the Pharmaceutical Society of Great Britain, the said Council doth hereby resolve and declare that the Schedule to the Poisons and Pharmacy Act, 1908, ought to be amended by the addition to Part I of the following words:
>
> Dinitro phenols; dinitro cresols; preparations or admixtures containing dinitro phenols; preparations or admixtures containing dinitro cresols."

The said Society, having submitted their resolution for the approval of the Privy Council, the Lords of the Privy Council signified their approval of the said resolution. (See *London Gazette*, April 13th, 1934.)

International Atomic Weights

FOURTH REPORT OF THE COMMITTEE ON ATOMIC WEIGHTS OF THE INTERNATIONAL UNION OF CHEMISTRY*

The report covers the 12 months ending September 30th, 1933. The atomic weight of carbon has been shown once more to be slightly higher than the official value 12·00, but no change is being made for the present. The eight following elements appear in the 1934 Table with modified atomic weights: (i) The atomic weight of potassium is now 39·096, as the result of numerous analyses of the chloride and bromide. (ii) The value for arsenic is slightly reduced to 74·91; as in the case of potassium this number was obtained by comparison with silver, arsenic trichloride and tribromide being used. (iii) Selenium was made to act on weighed quantities of the purest silver; the weight of the synthetic silver selenide led to the lower atomic weight 78·96, which has been adopted. (iv) Indium trichloride and tribromide were analysed, the atomic weight of indium being calculated at 114·76. (v) Tellurium was converted into tetrabromide, and this in turn into silver bromide. The higher figure, 127·61, is the mean of closely agreeing results obtained by the above method and the synthesis of silver telluride. (vi) Caesium chloride, spectroscopically free from rubidium and potassium, was converted into silver chloride; the value 132·91 is now adopted. (vii) Ytterbium chloride, purified by Prandtl and tested by *X*-ray analysis, was compared with silver; the atomic weight of ytterbium is now lowered to 173·04. (viii) Osmium, prepared from the re-distilled tetroxide, was re-oxidised, and the tetroxide was converted into ammonium chloro- and bromo-osmate. The pure dry salts were reduced in hydrogen, which was replaced by nitrogen before exposure of the metal to the air. The higher figure, 191·5, has been inserted in the Table.

Lead.—A number of careful determinations of the atomic weight of lead from various sources gave the following results:—Common lead, 207·211; from cyrtolite (New York State), 205·927; from Katanga pitchblende, 205·97; from Morogoro uraninite, 206·038; from Katanga curite, 206·031. The method adopted was conversion of lead chloride into the silver compound. W. R. S.

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* By G. P. Baxter (chairman), Mme Curie, O. Hönigschmid, P. Lebeau, and R. J. Meyer. Union Internationale de Chimie, Sécrétariat Général: 49, Rue des Mathurins, Paris.

Third International Technical and Chemical Congress of the Agricultural Industries

This Congress was held in Paris, from March 26th to March 31st, 1934, under the auspices of the French Ministry of Agriculture. Senator Fernand David, Member of the National Agricultural Academy of France, was President of the Congress, and Professor Joseph Pérard was President of the Executive Committee of the Congress. The social events included a reception, by the President of the Republic, of the foreign delegates to the Commission.

The set subjects down for discussion at the Congress were divided into the following five groups:—

Group I. Scientific and Economic Questions.—These included: (i) Determination of p_H and its value in the agricultural industries, (ii) Waste liquors, (iii) Utilisation of over-production of agricultural products, (iv) Improvement of the sugar beet and cane by genetic selection.

Group II. Sugar.—Subjects considered were: (v) Purification of sugar juices, (vi) Crystallisation of sugar, (vii) Storage of sugar.

Group III. Fermentation Industries.—The questions discussed were: (viii) Fermentation—in both its theoretical and practical aspects, (ix) Continuous diffusion, (x) The fruit juice industry.

Group IV. Food Industries, including: (xi) Qualities demanded in bread in different countries and the corresponding properties of flours and wheats, (xii) Evolution of plant used in the vegetable oil industries, (xiii) Use of vegetable oils in motors, (xiv) Collection, transport and treatment of milk, (xv) Cocoa and chocolate.

Group V. Allied Industries.—(xvi) Technique and economics of alcohol fuels and their use in different countries, (xvii) Wood distillation.

In addition to communications on the above subjects, papers dealing with analytical, technical and economic matters were read before the different sections.

It was decided that the next Congress be held in 1935 in Brussels, where there will be an Exhibition during that year, and that subsequent Congresses shall take place at intervals of three years.

The Society of Public Analysts and other Analytical Chemists was represented at the Congress by Mr. T. H. Pope.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs Analysis

Determination of Hydroquinone, especially in Salt Herrings. W. Preiss. (*Z. Unters. Lebensm.*, 1934, 67, 144–160.)—In the iodimetric determination of hydroquinone in small amounts, the use of potassium bicarbonate to render the solution alkaline causes inaccuracy, unless the liquid is previously saturated with carbon dioxide. Preferable is the use of either disodium phosphate or sodium acetate. Contrary to statements in the literature, quinone may be distilled unchanged in steam, provided that the solution is kept at a definite p_H value. Hydroquinone is now added to salt herrings to delay their alteration, and the following methods have been elaborated to detect and determine this substance in the pickling brine and in the fish.

If hydroquinone has been used, the separated brine shows very little fat and has a deep-red colour, even when all the hydroquinone has undergone change.

About 150 grms. of the well-mixed brine are weighed—soon after the separation—in a 200-ml. flask, and 15 ml. each of about 30 per cent. acetic acid solution, 5 per cent. potassium ferrocyanide solution and 10 per cent. zinc sulphate solution are added. The liquid is made up to 200 ml. with water, well shaken, and, after a time, filtered through a dry filter into a dry vessel, the first few ml. of the filtrate being discarded. When a little of the liquid (A) is poured down the wall of a test-tube containing a solution of silver nitrate in excess of ammonia solution, the zone of separation becomes red or violet-red if small amounts of hydroquinone are present; with larger amounts (a few mgrms.), a brownish-black precipitate appears on mixing the two layers. If quinone is present, addition to the filtrate of an acidified potassium iodide solution containing starch produces at once a blue colour.

To determine hydroquinone in the brine, 100 ml. of the clear filtrate (A) are placed in a distilling flask with 3 ml. of 5 per cent. sulphuric acid, 5 ml. of glacial acetic acid, 40 grms. of sodium chloride, and 10 ml. of ferric chloride solution (about 30 per cent.). The condenser-tube is fitted with an adapter dipping into a Sendtner flask (as used for the determination of iodine value) containing about 5 ml. of 0·1 *N* sulphuric acid and 15 ml. of water. The distillation is carried out in a current of steam, and is continued until all the quinone has passed over, the collection of 100 to 150 ml. of distillate usually sufficing. The distillate is treated with about 1 to 1·5 grm. of potassium iodide and 5 to 10 ml. of dilute sulphuric acid and, after standing for a short time in the closed flask, is titrated with 0·02 *N* sodium thiosulphate solution, starch being added towards the end of the titration. Multiplication by 1·145 of the number of ml. of the thiosulphate used gives mgrms. of hydroquinone in the filtrate used; this factor allows for the fact that only 96 per cent. of the total hydroquinone is recovered by the above procedure. Excessive frothing during the distillation may be overcome by passing carbon dioxide through a tube ending just below the neck of the distilling flask.

The presence of hydroquinone and quinone in the herrings themselves may be detected by subjecting a cold absolute alcohol extract of the herrings to the reactions used for the brine. In no case has quinone been found in herrings salted with a mixture of hydroquinone and rock-salt. To determine the hydroquinone, 100 grms. of the minced and mixed herrings are ground in a glazed mortar with 150 grms. of anhydrous sodium sulphate. The mixture, together with exactly 200 grms. of absolute alcohol, is transferred to a 500-ml. Sendtner flask, which is vigorously shaken at short intervals during 1 to 1½ hour. The mass is then filtered through a dry pleated filter into a weighed flask, and the whole of the clear filtrate (120 to 140 grms.) is transferred to a distilling flask with the aid of a little alcohol, treated with 0·5 to 1 ml. of 5 per cent. sulphuric acid, and distilled from a boiling water-bath and in a current of carbon dioxide until 15 or 20 ml. remain. This is allowed to cool somewhat in the gas stream, and is then treated with 5 ml. of glacial acetic acid, 50 grms. of sodium chloride, 7 to 8 ml. of about 30 per cent. ferric chloride solution and sufficient water to bring the volume up to 150 or 200 ml. The subsequent procedure is as described above for the determination of hydroquinone in the brine. The sample of herrings to be examined should be taken from the brine-covered lower layers of the cask, and the extraction with alcohol should be carried out as soon as possible after the sampling. During storage of the herrings, their content of hydroquinone diminishes owing to oxidation to quinone and interaction of this with the constituents of the herrings. T. H. P.

Phosphatids of Wheat Flour. F. E. Nottbohm and F. Mayer. (*Z. Unters. Lebensm.*, 1934, **67**, 369–379.)—The authors have found previously (*ibid.*, 1933, **65**, 55) that only one-half as much choline is obtainable from cocoa beans by direct extraction with alcohol as by the magnesia process, which is now modified as follows to apply to material rich in starch:—Ten grms. of the material (flour) are thoroughly ground with 2 grms. of calcined magnesia, and the whole is mixed with a little water to give a uniform paste. This is washed into a 300-ml. Erlenmeyer flask to a total volume of about 150 ml., and is heated for an hour in a briskly-boiling water-bath. The swollen mass is cooled, transferred to the mortar originally used, and mixed gradually with alcohol, 150 ml. of which are added in all. The clear supernatant liquid is poured off, and the precipitate is centrifuged to recover the rest of the alcoholic solution. The solid residue still retains about 5 per cent. of the total choline, which may be extracted by repeating the treatment with magnesia and alcohol. The combined alcoholic extracts are evaporated to about 50 ml. with hydrochloric acid and are prepared for the determination of the choline by heating in an autoclave (ANALYST, 1932, **57**, Abst., 322).

Examination in this way of the various constituents of wheat flour shows that the gluten contains little choline and the wash-water rather more, the main quantity being in the starch washed away. The choline is present in the flour, not as free base, but as choline-lecithin. The wheat phosphatid has the P : L number (ANALYST, 1934, Abst., 182) 1·56, and contains about 26 per cent. of carbohydrate, calculated as glucose, but the starch washed out from the flour appears to be free from carbohydrate. The amount of phosphatid found in wheat flour is about three times that formerly assumed, and the proportion in bran is still greater. Trigonelline is not present either in flour or in bran. T. H. P.

Investigation of Peas. R. Neseni. (*Z. Unters. Lebensm.*, 1934, **67**, 195–197.)—A number of samples of peas, both in the pod and shelled, were examined. Most of the samples failed to comply with the requirements of the *Codex alimentarius austriacus* with regard to colour, odour, regularity, freedom from borers, age, and impurities (cankered, broken or immature peas, foreign seeds, insects, straw, soil, stones, etc.). Both yellow and green peas in the pod showed higher percentages of altered seeds than the shelled wares, but these contained the higher proportions of partly eaten and broken peas. Examination in ultra-violet light revealed, with many of the samples, the presence of points or spots either black or showing intense sulphur-yellow fluorescence; these points or spots are produced by either bacteria or moulds and indicate damp storage. T. H. P.

Changes in the Composition of the Potato during Winter Storage. L. Erdős. (*Z. Unters. Lebensm.*, 1934, 67, 198–202.)—A number of kinds of potatoes, specially suitable for growing in the dry climate of Hungary, were examined in December, 1931, and, after storage in a cool, dry place, in April and June, 1932. During the storage, the specific gravity mostly increased steadily, the extent of the increase varying with the kind. With some sorts the specific gravity was lower in June than in April, the loss of moisture and dry matter being unaccompanied by the shrinking which usually occurs. In relation to the dry matter, the ash increases during storage, and the protein increases both in the tuber and in the germ. Neither the starch-content nor the proportion of dry matter runs parallel with the specific gravity, and Maercker's table for determining starch or dry matter should be used only when results are required quickly, and then only for ripe potatoes. Far more accurate results are furnished by the protein- and salt-free extractives, which contain little but the starch. T. H. P.

Iodine-Content of Pennsylvania Potatoes. D. E. H. Frear. (*J. Agric. Res.*, 1934, 48, 171–182.)—The iodine in 135 samples of potatoes from different parts of Pennsylvania was determined by means of a modification of the closed combustion method of Karns (*Ind. Eng. Chem., Anal. Ed.*, 1932, 4, 299, 375), in which carbon dioxide gas was used, and the absorption vessel consisted of a Witt filtering apparatus, with three thicknesses of filter-paper or paper towelling within the ground-glass joint sufficiently porous to allow the passage of the gases, but condensing and retaining the iodine. The minimum iodine-content was 10 parts, the maximum 216 parts, and the mean 77·8 parts per billion, expressed on a moisture-free basis. The mean iodine-content of potatoes grown in the north-central part of the State was considerably lower than that for the other localities, but, although potatoes grown on glaciated soils contained slightly more iodine than those from non-glaciated soils, no significant differences could be correlated with type of soil; nor did the use of fertilisers affect the iodine-content. Two samples from a marine soil, however, had a high iodine-content. No correlation was found between the size or variety of potato and iodine-content, nor could incidence of goitre be related in any way to the proportion of iodine. D. G. H.

Merck's Diastase, a Proposal for Barley Analysis. W. Piratzky. (*J. Inst. Brewing*, 1934, 40, 175–176; *Woch. Brau.*, 1934, 51, 33–34.)—Merck's new "Diastase reinst, Art. No. 3029" is suggested as preferable to a freshly-prepared malt-extract for standardisation of the method of digesting and saccharifying barley. It is stated to be prepared by precipitation with absolute alcohol of extracts of malt in dilute alcohol, and it contains water, 9 to 10 per cent.; ash, 10·4; nitrogen, 7·75 (corresponding with 48·4 per cent. of protein); and sugar (as maltose), 25·5 per cent.; the remaining 15·7 per cent., presumably, represents dextrins, and there is a small quantity of flocculent matter insoluble in water, due probably to protein denatured by drying. The diastatic activity is 10 times that of a pale malt, and 100 ml. of a 1·3 per cent. solution are sufficient for a determination of the extract in barley, and give results in close agreement with those obtained by means of the usual malt extracts. Solutions of this strength show a loss in activity of only 2 per cent. after 2 months in an ice-chamber if stored in sterile 100-ml. bottles, each containing a few drops of a mixture of 1 part of chloroform with 2 parts of acetone. J. G.

Determination of Carbon Dioxide in Beer. J. L. Baker and H. F. E. Hulton. (*J. Inst. Brewing*, **1934**, **40**, 171–173.)—The method, which is more suitable for routine purposes than the gasometric procedure previously described (*ibid.*, 1923, **29**, 427), but is not applicable to black beers, depends on the addition of known volumes of boiled and unboiled beer to an excess of a standardised (approximately 0·2 *N*) solution of barium hydroxide. Since boiling removes carbon dioxide, the difference between the back-titrations with 0·5 *N* oxalic acid is a measure of the carbon dioxide content (1 ml. of oxalic acid = 0·011 grm. of CO_2). Exactly 50 ml. of the baryta solution are measured into a flask with a long neck near the middle of which is a 70 ml. mark, with graduations at 0·5-ml. intervals above and below this, and about 20 ml. of the beer are then cautiously run in through a tube which reaches to the bottom of the bottle, the exact volume added being determined from the graduations on the neck. The mixture is washed into a flask with cold distilled water, and is titrated in the presence of 20 ml. of approximately 1·0 *N* barium chloride solution with the oxalic acid, phenolphthalein being used as indicator and the mixture being well shaken and kept cooled before and during the operation. Another 20-ml. portion of the beer is then well roused and boiled with 50 ml. of water until all carbon dioxide is expelled, a reflux condenser being necessary if the acidity (as acetic acid) exceeds 0·1 per cent., in order to avoid loss of acid; the solution is then cooled, and the baryta equivalent of the sulphates and phosphates in the beer is determined by repetition of the above titration. If the errors in the measurement of the volume of beer and in the titration are 0·1 and 0·2 to 0·3 ml., respectively, the error in the volume of carbon dioxide may attain 50 ml. per litre, or about 2·6 per cent. of the total volume; this is considered sufficiently accurate for routine work, and compares favourably with the accuracy obtained by removing the gas by boiling and weighing it after absorption in soda-lime. If the beer is in a pressure-tank, it must be transferred without loss of gas to a half-pint bottle fitted with a metal screw-stopper carrying two tubes, each provided with a valve (*e.g.* a motor-car petrol cock); one reaches nearly to the bottom of the bottle, whilst the other is shorter and projects just inside the stopper. The bottle is cooled in ice, the former (longer) tube is connected with the tap on the tank which is then opened, the valve on the longer tube then being also opened so that beer and froth partly fill the bottle. The second valve is then opened slightly so that the beer escapes slowly, and after 10 minutes under these conditions both cocks are closed again. If the beer is already in bottle, a similar procedure may be used to transfer it to the measuring flask, the bottle being clamped in an inverted position and fitted with a rubber stopper carrying two glass tubes, each provided with a pinch-cock. J. G.

Frozen Wine. A. Heiduschka and C. Pyriki. (*Chem.-Ztg.*, **1934**, **58**; 229.)—A process for the treatment of fruit wine on the large scale involves the freezing of the wine and separation of the solid and liquid portions by means of a centrifuge (see D.R.P., 163,101, 23rd Nov. 1902). In the present experiments the wine was immersed in a mixture of ice and salt until it became pasty, and was filtered on a cooled funnel; the first runnings were then frozen and re-filtered. The analyses are given below, columns (*a*) and (*b*) referring to a German white and red wine, respectively. They show, on the whole, that the constituents of the wine tend to accumulate in the unfrozen portions (*cf.* O. Reinke, *ibid.*, 1934, **58**, 17; and P. Walden, *ibid.*, 1934, **58**, 96). The taste of these portions had deteriorated, and the bouquet was lost.

Constituent	Original wine (grms. per litre)		Liquid portion (grms. per litre)				Thawed expressed residue (grms. per litre)			
			First		Second		First		Second	
	a	*b*	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*
Sp.gr. at 4° C. ..	0·9934	0·9955	0·9924	0·9956	0·9913	0·9954	0·9946	0·9960	0·9937	0·9962
Alcohol	77·00	84·60	101·10	99·70	113·10	116·10	59·10	66·90	77·00	72·90
Extract	18·20	26·20	24·40	32·50	28·10	37·60	14·40	21·60	19·00	24·20
Ash ..	1·85	2·95	2·45	3·70	2·50	4·57	1·44	2·58	1·85	3·05
Total acids	7·24	7·12	9·37	8·66	10·57	10·20	5·77	5·89	7·50	6·32
Volatile acids	0·67	1·28	0·70	1·44	0·76	1·47	0·39	0·86	0·69	1·02
Titrated non-volatile acids	6·41	5·52	8·49	6·86	9·62	8·36	5·28	4·81	6·64	5·04
Lactic acid	3·82	2·80	5·04	3·17	5·59	3·95	3·36	2·24	3·95	2·64
Tartaric acid	2·33	1·99	3·11	2·39	3·22	2·97	1·69	1·50	2·40	1·50
PO_4'''..	0·25	0·26	0·29	0·30	0·34	0·36	0·18	0·20	0·23	0·25
Sugar ..	1·29	2·49	1·60	3·08	1·81	3·64	1·02	2·24	1·38	2·38
Glycerol	4·91	6·85	6·86	7·78	8·98	8·47	4·03	5·87	5·80	6·74

J. G.

Reif's Colour Reaction for the Detection of Benzylidenesorbitol. H. Kreipe. (*Z. Unters. Lebensm.*, 1934, **67**, 426–428.)—This reaction (ANALYST, 1934, Abst., 44) may be relied on to detect sorbitol in wine or wine vinegar, provided that special attention is paid to certain details of the procedure. The benzylidenesorbitol to which the colour-test is applied must be as pure as possible. Even traces either of the yeast used to ferment the residual sugars of the wine or of the decolorising charcoal employed exert a disturbing effect on the colour reaction. The charcoal is best removed by filtration through a layer of Seitz filtering-material on a porcelain thimble. Purification of the precipitated benzylidenesorbitol by means of petroleum spirit, either alone or mixed with alcohol, must result in the removal of all traces of benzaldehyde. To exclude the possibility of benzylidenemannitol taking part in the colour reaction, A.R. sulphuric acid of sp.gr. 1·84 should be used, and care must be taken that none of this acid adheres to the wall of the test-tube. Drying of the precipitate at 75° to 80° C. must not be omitted, since a trace of residual moisture would alter the concentration of the acid, and consequently the solubilities of the benzylidene derivatives. Colour reactions, being subjective, are not suitable for forensic purposes, and the preparation of hexa-acetylsorbitol (*cf.* Jahr, ANALYST, 1930, **55**, Abst., 452), which can be exhibited, is then of advantage in proving the presence of sorbitol in a wine or wine vinegar. T. H. P.

Composition of Oil of Carrots. L. Palfray and (Mlle) A. M. Lepesqueur. (*Compt. rend.*, 1934, **198**, 1365–1367.)—This oil, obtained by steam distillation, is free from methoxy and ethoxy groups and nitrogen, and contains at most traces of phenols. It shows no fluorescence in ultra-violet light, fixes bromine in chloroform solution, and gives a yellow colour with antimony trichloride (*cf.* Sabetay, ANALYST, 1933, **58**, Abst., 712). The constants are: Sp.gr. 0·9413 at 17°/4° C., $n_D^{18·5}$ 1·4931 $(\alpha)_D^{17}$ + 3·90°, acid value 3·47, saponification value 19·73, or, after acetylation, 55·5. The oil combines to a small extent with sodium bisulphite, but no definite oxime or semicarbazone could be isolated. The free acids present comprise formic and acetic acids. Other constituents detected were (1) *l*-pinene, and (2) an unsaturated compound, $C_{15}H_{26}O$, apparently identical with Asahina and Tsukamuto's carotol (*J. Pharm. Soc. Japan*, 1925, [525], 1), which fixes one molecule of hydrogen in presence of oxidised platinum and appears to contain one hydroxyl group. T. H. P.

Determination of Chlorogenic Acid in Coffee. C. Griebel. (*Z. Unters. Lebensm.*, 1934, **67**, 452–456.)—Hoepfner's statement that treatment of coffee with steam prior to roasting diminishes the content of chlorogenic acid (ANALYST, 1933, **58**, Abst., 100, 702; Plücker and Keilholz, ANALYST, 1933, **58**, Abst., 701; and *Chem.-Ztg.*, 1933, **57**, 875) is further discussed (ANALYST, 1933, **58**, Abst., 621). Roasting diminishes the content of chlorogenic acid of coffee by an amount depending on the degree of roasting. If Hoepfner's statement is correct, steam-treated coffees should show, after roasting, lower proportions of this acid than ordinary roasted coffees; this is, however, usually not so. The slight differences in this direction sometimes observed may well have been due to somewhat more intense roasting of the steam-treated coffees. T. H. P.

Study of Aloes and Determination of some of its Constituents. P. Valaer and G. E. Mallory. (*Amer. J. Pharm.*, 1934, **106**, 81–96.)—When drugs such as rhubarb, cascara, frangula, senna and aloes, whose action is determined mainly by resinous hydroxyanthraquinone compounds and other anthraquinone derivatives, are extracted with ether in presence of acid, and the ethereal extract is made strongly alkaline with ammonia, a red colour develops. This test may be used as the basis of the determination of aloes in medicinal preparations. Under controlled conditions, the depth of the colour varies almost directly in proportion to the amount of aloes or other emodin-bearing drug present. In this way the proportion of free emodin bodies is obtained. A similar determination, carried out after hydrolysis with concentrated sulphuric acid, gives the total emodin bodies, the colour being then due to both free and combined anthraquinone compounds. The colours are compared with those obtained in the same way from aloes, and, in view of the wide variations shown by aloes of different origins, it is suggested that only those from Curaçao, which have a high aloin-content, be regarded as official.

In a second colorimetric method, for determining emodins in presence of phenolphthalein, the preparation is treated with ammonia and benzyl alcohol, and the colour developed is measured as before. Whichever method is used, the colour is suitably expressed in terms of the Lovibond red and yellow glasses, and tables are given showing the results thus furnished by aloes of the three recognised varieties, namely, Socotrine (E. Africa), Cape, and Curaçao. Shaffer's gravimetric determination of aloin is satisfactory when applied to about 50 grms. of aloes, but becomes unreliable with preparations containing, together with other drugs and aromatics, only 4 to 8 grains of aloes per fluid oz. Hager's method is not trustworthy, even with pure aloes, and is still less so with preparations containing invert sugar, etc. T. H. P.

Differentiation Reactions of Argyrol, Collargol, Electrargol, and Protargol. C. Vaille. (*J. Pharm. Chim.*, 1934, **126**, 256–261.)—In order to differentiate the various silver colloids or hydrosols present in a solution, it is necessary to arrange that the concentration of the colloidal silver shall be about 0·07 to 1 per cent. To 2 ml. of a 0·5 per cent. solution of chromic acid is added sufficient of the colloidal solution to give, after shaking, the yellow colour of the chromic acid, more of the solution being used when it is necessary to dilute, so that for a 0·07 per cent. solution, 7 ml. are taken, and for a 1 per cent. solution only 1 ml. From 0·5 to 1 ml. of a saturated solution of sodium carbonate is then added. With argyrol and protargol the first precipitate re-dissolves, but with collargol and electrargol the addition of the alkali to the liquid produces a brick-red precipitate which is clear at first. To differentiate argyrol from protargol, about 9 ml. of silver solution are added to 1 ml. of a 10 per cent. solution of sodium hyposulphite, followed by 3 drops of phenolphthalein solution. In the presence of protargol a rose to red colour results, whilst with argyrol the colour is masked by that of the argyrol itself. To differentiate collargol from electrargol, 5 ml. of the silver solution are added to a mixture of 0·5 ml. of the 0·5 per cent. chromic acid solution and 5 ml. of nitric acid (French Codex). After 24 hours, and often before, the yellow colour of the liquid is replaced by a bluish tint in the presence of electrargol, but no change occurs with collargol. Also, if equal parts of a saturated solution of picric acid and the silver solution are mixed, collargol will give a precipitate after 1 hour, whilst electrargol will not. D. G. H.

Biochemical

Daily Administration of Small Quantities of Aluminium in relation to the Development of Cancer. G. Bertrand and P. Serbescu. (*Compt. rend.*, 1934, **198**, 1100–1102.)—Two series of rabbits were treated, the first by administration of tar alone, and the second by tar in combination with 6 weekly doses of 20 mgrms. of aluminium, given as sulphate. In the first series 78·3 per cent. of the animals living over 40 days died of cancer, and in the second series 50 per cent. In no case where aluminium had been given were any lesions of the stomach or digestive tract found, and even one rabbit which received 50-mgrm. doses per kilo. of body weight over a period of 60 days, produced a litter of six after 28 days. From the 60th day onwards it was also treated with tar and died of broncho-pneumonia on the 162nd day. Its digestive tract was normal. It is concluded that the facts do not support the alleged toxicity of aluminium, and that there is no evidence that the ingestion of aluminium is favourable to the development of cancer. D. G. H.

Evaluation of the Quality of Meat by Artificial Digestion with Pepsin. J. A. Smorodinzew. (*Z. Unters. Lebensm.*, 1934, **67**, 429–432.)—For this purpose use is made of a 0·5 to 1 per cent. solution of an active pepsin containing sufficient hydrochloric acid to make the p_H value of the solution 1·5 to 1·7. The chopped meat (1 grm.) is digested with 10 ml. of the enzyme solution for 3 hours at 37° C. The extent to which digestion has proceeded is then measured by formol titration of the solution with 0·5 *N* sodium hydroxide solution. Muscle fibre or meat containing it in large proportion is found to be more readily digestible (by 25 to 30 per cent.) than connective tissue or meat consisting largely of this.

T. H. P.

Quantitative Determination of Glutathione. L. Binet and G. Weller. (*Compt. rend.*, 1934, **198**, 1185–1187.)—The method for determining glutathione in vegetable or animal tissue depends on its quantitative precipitation by cadmium lactate in a medium of p_H 6 to 7, without oxidation of the sulphydryl group. One to 2 grms. of the tissue are cut up and weighed in a tared receptacle containing 5 ml. of 10 per cent. trichloroacetic acid. The tissue is ground with sand, triturated with the acid and a further 5 ml. of acid are added. After 3 to 5 minutes the mass is filtered, the extract is placed in a centrifuge tube, and the extraction is repeated 3 times. Three to four drops of bromthymol blue are added to the united extracts, which are neutralised by first adding a 50 per cent. (by vol.) solution of sodium hydroxide, with constant shaking, and when neutralisation is nearly complete finishing with a 2 per cent. (by vol.) solution of sodium hydroxide until a blue tint, which is stable for about 2 minutes, is formed on adding 1 drop of the alkali. Two ml. of a 1 per cent. solution of cadmium lactate are then added, followed by 1 or 2 drops of the 2 per cent. sodium hydroxide solution, which turn the yellow or green solution back to blue. These operations should not have taken more than 1 hour from the death of the animal. The flocculated precipitate is formed in 1 to 2 hours, and the mixture is then centrifuged at a high speed. The supernatant liquid is decanted, the precipitate is dissolved in 10 ml. of 10 per cent. trichloroacetic acid, and the solution is titrated with a 0·004 *N* solution of iodine in the presence of starch. The necessary correction is found by determining the volume of the iodine solution required to give the first indication of colour with starch in 10 ml. of the trichloroacetic acid. In 32 assays the results varied between the extremes of 98 and 104 per cent., and in determining the addition of pure glutathione to extracts of different tissues the results were 99·31 per cent. for liver extract, 98·48 for suprarenal gland, 100·6 for spleen, and 98·5 per cent. for pancreas extracts. Figures obtained for the organs of the dog were lower than those found by the usual methods, and (as mgrms. per 100 grms. of fresh tissue) averaged: Liver, 130; suprarenal gland, 114; spleen, 102; pancreas, 97; and cardiac muscle, 62.

D. G. H.

Simple Adaptation of Kolthoff's Colorimetric Method for Determination of Magnesium in Biological Fluids. A. D. Hirschfelder and E. R. Serles. (*J. Biol. Chem.*, 1934, **104**, 635–645.)—The magnesium ions of the plasma can be determined colorimetrically with titan yellow or Clayton yellow in alkaline solution after the calcium has been precipitated as oxalate; a pink colour is produced. This method avoids the necessity of precipitating the magnesium either as the phosphate ($MgNH_4PO_4$) or as the hydroxyquinoline compound, and is, therefore, much simpler and much more rapid than the methods previously used. *Reagents required.*—All reagents used must be free from magnesium and calcium, *i.e.* they must give no trace of pink when tested with sodium hydroxide solution plus a drop of the dye (titan yellow or Clayton yellow), and no precipitate or turbidity on addition of ammonium oxalate. (i) Sodium hydroxide solution approximately 0·4 *N* (1·6 per cent.) concentration. (ii) Dye solution: titan yellow or Clayton yellow, 0·01 grm. per 100 ml. of water. (iii) Ammonium oxalate: 3 grms. per 100 ml. (iv) Colloid-dispersing agent. An approximately 0·5 per cent. suspension of ordinary soluble starch or pure dextrin may be used. *Standard Magnesium Solutions.*—For magnesium determinations the colour produced by diluted alkalised plasma or urine is compared with that produced by 0·0002 per cent. of magnesium. *Standard* 1.—A permanent standard solution containing 0·1 per cent. of magnesium is prepared by dissolving 1 grm. of powdered magnesium in 5 ml. of concentrated hydrochloric acid and diluting with water to 1000 ml. It is preserved by adding 2 ml. of chloroform. *Standard* 2.—Two ml. of standard 1 are diluted to 100 ml. To 1 ml. of the diluted standard are added 7 ml. of colloid-dispersing agent, 1 ml. of 0·01 per cent. titan (or Clayton) yellow solution and 1 ml. of 0·4 *N* sodium hydroxide solution. The tube is stoppered and the contents mixed by inversion. This standard must be freshly prepared; 1 ml. of the mixture ≡ 0·002 mgrm. of magnesium.

Analytical Procedure.—About 5 ml. of blood are placed in a 15-ml. centrifuge tube containing a few small crystals of sodium citrate. The tube is closed with a rubber stopper, inverted three times to mix the contents, and centrifuged at 1500 to 1800 R.P.M. for 15 minutes. One ml. of the plasma is pipetted off into another (graduated) centrifuge tube, 0·5 ml. of 3 per cent. ammonium oxalate solution is added, and then 8·5 ml. of water at 45° C. The tube is stoppered, inverted, kept in a water-bath at 45° C. for 20 minutes, and then centrifuged for 15 minutes. The calcium oxalate precipitate is used for the determination of calcium by the Kramer–Tisdall method (*J. Biol. Chem.*, 1921, **47**, 475). For the determination of magnesium 5 ml. of the supernatant fluid (= 0·5 ml. of plasma) are pipetted off into a test-tube, 3·0 ml. of dispersing colloid are added, and then 1·0 ml. of dye solution and 1 ml. of 0·4 *N* sodium hydroxide solution. The contents are mixed and compared in a colorimeter with standard 2. The light used should be filtered through a colour screen of 0·01 per cent. dye solution. The calculation is (reading of standard/reading of unknown) × 4 = mgrm. of magnesium per 100 ml. of plasma. If the magnesium-content is too high the mixture must be diluted. A micro-method is described for the accurate determination of magnesium and calcium in 0·1 ml. of plasma. The colorimetric method can be used for the determination of magnesium in urine, if the phosphates are first separated by precipitation with uranyl acetate. P. H. P.

Reaction of Nitrous Acid with Cystine and Related Sulphur-containing Compounds. S. A. Lough and H. B. Lewis. (*J. Biol. Chem.*, 1934, **104**, 601–610.)—In an effort to explain the anomalous behaviour of cystine in the Van Slyke gasometric method for amino nitrogen noticed by Van Slyke (*J. Biol. Chem.*, 1911, **9**, 185), and further investigated by Schmidt (*J. Biol. Chem.*, 1929, **82**, 587), a study was made of the reaction of a series of sulphur-containing compounds with nitrous acid. Attempts were made to approach the problem of the reaction between cystine and nitrous acid by securing data along three related lines: (i) When cystine is acted upon by nitrous acid, what degree of oxidation of the sulphur can be obtained? (ii) By the examination of a series of organic compounds in which the type of sulphur linkage varies, is it possible to establish any relationship between the oxidation of the sulphur to sulphate by nitrous acid and production of extra nitrogen in the Van Slyke reaction? (iii) What is the chemical nature of the gas produced when nitrous acid reacts in the Van Slyke apparatus with a nitrogen-free sulphur-containing compound of known purity, the sulphur of which is readily oxidised to sulphate by nitrous acid? The experiments show that the sulphur of cystine was oxidised rapidly to sulphate by nitrous acid, but it was impossible to effect the oxidation of more than 85 per cent. of the sulphur, even over a period of 144 hours, and with the frequent addition of a fresh supply of the oxidising agent. Evidence was obtained to support the contention of Schmidt that the extra nitrogen produced in the reaction between cystine and nitrous acid is related directly to the oxidation of the sulphur to sulphate with the reduction of nitrous acid to nitrogen. When thioglycollic acid reacted with nitrous acid, the gas not absorbed by the alkaline permanganate in the Van Slyke determination was shown by spectroscopic examination to be nitrogen. Since thioglycollic acid resembles cystine in the Van Slyke reaction, in that extra nitrogen is produced and the sulphur is rapidly oxidised to sulphate, it is believed that the "extra nitrogen" in the reaction between cystine and nitrous acid is in reality nitrogen, formed as a result of the reduction of the acid simultaneously with the oxidation of the sulphur. P. H. P.

Oxidation of Amino Acids by means of Silver Oxide. R. M. Herbst and H. T. Clarke. (*J. Biol. Chem.*, 1934, **104**, 769–788.)—In the course of the preparation of dimethylglycine from its hydrochloride it was observed by Clarke, Gillespie and Weisshaus (*J. Amer. Chem. Soc.*, 1933, **55**, 4571) that addition of excess of silver oxide to a cold aqueous solution of the latter caused the evolution of carbon dioxide, accompanied by the odours of dimethylamine and formaldehyde. Repetition of this experiment at the boiling temperature showed that the following reaction takes place, with essentially quantitative yields:

$$(CH_3)_2NCH_2CO_2H + 3Ag_2O = (CH_3)_2NH + 2CO_2 + H_2O + 6Ag.$$

As this reaction, if general, might offer certain analogies to the biochemical oxidation of amino acids, its study was extended to other compounds. The results of a series of qualitative tests are shown in a table. The following conclusions are reached:—α-Amino acids are oxidised in hot aqueous solution by silver oxide, with the formation of ammonia, carbon dioxide and aldehydes; the latter may undergo further oxidation to the corresponding acids to an extent depending upon experimental conditions and the volatility and solubility of the aldehyde. Replacement of both amino hydrogen atoms by methyl groups facilitates rather than inhibits the oxidisability, but in betaine this faculty is entirely lost. The presence of hydrogen at the α-carbon atom is not essential to oxidisability. Acylation of the amino group tends to prevent oxidation, but this effect is by no means universal.

P. H. P.

Reaction of Cholesterol with Sulphuric, Selenic and Telluric Acids. E. Montignie. (*Bull. Soc. Chim.*, 1933, **53–54**, 1394.)—(i) On replacing sulphuric acid by concentrated selenic acid in Liebermann's reaction cholesterol gives a pale green colour in 4 or 5 minutes, darkening to a maximum intense green in 30 minutes, whilst the colour disappears on the addition of water. The same reaction occurs very slowly with metacholesterol and stigmasterol. No colour results with a 50 per cent. solution of telluric acid. (ii) If sulphuric acid is added to a solution of cholesterol in chloroform, a red colour is formed (Salkowsky's reaction); selenic acid produces, in a few minutes, a red ring at the point of separation of the liquids; on shaking, the supernatant liquid becomes pink, and at the end of half an hour, brown, and the bottom layer turns pink. With telluric acid the reaction is negative. (iii) In the cold, concentrated sulphuric acid colours cholesterol crystals red; selenic acid makes them grey to greenish-black, and telluric acid gives no colour. (iv) On shaking 50 per cent. sulphuric acid with cholesterol at 100° C. for 1 hour, a mixture of cholesterylenes results, but with 45 per cent. selenic acid only a slight red colour is produced, and the cholesterol is unchanged. With telluric acid no reaction occurs in 1 hour, but if one molecule of the crystallised acid is intimately mixed with 1 of cholesterol and the mixture is kept at 170° to 180° C. for 30 minutes, the mass becomes brown; by taking up the mass with water and then alcohol most of the cholesterol may be recovered unchanged, but on dissolving the mass in benzene a tellurate separates. On evaporating the solvent, dissolving the residue in ether, and adding 95 per cent. alcohol to the solution, 10 per cent. of a white precipitate of cholesterylene (m.pt. 188° to 193° C.) is formed. D. G. H.

Action of Iodine on Cholesterol. E. Montignie. (*Bull. Soc. Chim.* 1933, **53–54**, 1412–1414.)—If increasing quantities of iodine are allowed to react with a molar solution of cholesterol dissolved in various organic solvents, by boiling the mixture for one hour and evaporating it on a water-bath, various mixtures of iodine compounds, very difficult to separate, are formed. If, however, instead of evaporating the mixture on a water-bath, the chloroform or benzene solution is treated by repeated washings with sodium thiosulphate, all the iodine which has not reacted with the cholesterol is removed. If the solvent is then evaporated and the residue is taken up with boiling alcohol, a non-saturated black residue remains. The alcoholic solution deposits crystals, which, after several re-crystallisations, melt at 139° to 142·5° C., and consist of a non-saturated substance which takes up bromine in an ethyl acetate medium, giving a mixture of bromides. Acetic anhydride gives a mixture of acetates, the first crystals melting at 92°–95° C., and the last at 105°–110° C. Liebermann's reaction is positive, and the substance, in fact, behaves as a mixture of isomers of cholesterol, probably cholesterol and metacholesterol (m.pt. 139° C.). Allocholesterol is absent, and on treatment with sodium and amyl alcohol the mixture once more yields cholesterol (m.pt. 145° C.). D. G. H.

Contributions to the Study of Marine Products. III. Chemistry of Ostreasterol. W. Bergmann. (*J. Biol. Chem.*, 1934, **104**, 553–557.)—Bergmann (*J. Biol. Chem.*, 1934, **104**, 317; ANALYST, 1934, 294) described the isolation and properties of a new sterol, ostreasterol, which occurs in the oyster and other molluscs, contains two double bonds, and to which the formula $C_{27}H_{44}O$ was attributed. When subjected to catalytic hydrogenation, ostreasteryl acetate adds 2 molecules of hydrogen and becomes saturated. The determination of the equivalent weight of ostreasterol acetate by saponification gave values which agreed very well with the formula $C_{29}H_{47}O.CO.CH_3$. Therefore the formula for ostreasterol has to be changed from $C_{27}H_{44}O$ to $C_{29}H_{48}O$. The properties of ostreastanol acetate and of ostreastanol, $C_{29}H_{51}O$, were similar to those recorded for sitostanol and sitostanol acetate. Ostreastanol was, therefore, compared, side by side, with a pure sitostanol. The acetates, phenylurethanes and ketones were also compared. From the properties obtained, shown in a table, it is seen that ostreastanol must be considered as identical with sitostanol. The data obtained for ostreastanol are as follows:—Sterol, m.pt., 141° C., $[\alpha]_D = +23{\cdot}73°$; acetate, m.pt., 137° C., $[\alpha]_D = +14{\cdot}58°$; phenylurethane, m.pt., 175° C., and ketone, m.pt., 157° C., $[\alpha]_D = +41{\cdot}95°$. It was previously suggested that a tribromo-ostreasteryl acetate described might consist of a mixture of 1 molecule of a dibromide and 1 molecule of tetrabromide. This seems to be the case, for if bromine is added in a larger excess, and the mixture is left standing for a longer time, a well-crystallised bromide is obtained, which melts at 150·5° C., and yields a tetrabromide $C_{31}H_{50}O_2Br_4$; this is further proof that ostreasterol contains two double bonds. Ostreasterol is isomeric with stigmasterol, but, on catalytic reduction the latter yields stigmastanol (m.pt., 134–134·5° C.); thus a difference in the structure of the two sterols is clearly indicated. Cholesterol is regarded as the typical sterol of the animal kingdom. The fact that ostreastanol is identical with sitostanol must be regarded as very significant, because this is the first time that a sterol obtained from animal sources has been converted into a typical plant sterol. It raises the question whether any strict line can be drawn between zoosterols and phytosterols.

P. H. P.

Glucoreductone for the Standardisation of 2, 6-Dichlorophenolindophenol Solutions used for the Determination of Ascorbic Acid (Vitamin *C*) Z. I. Kertesz. (*J. Biol. Chem.*, 1934, **104**, 483–485.)—A simple method is presented for the standardisation of the indophenol indicator solution which was proposed by Tillmans, Hirsch and Hirsch (*Z. Unters. Lebensm.*, 1932, **63**, 1; *cf.* ANALYST, 1932, **57**, 260) for the quantitative titrimetric determination of ascorbic acid. Glucose solution heated under standard conditions develops a reproducible reducing capacity towards 2, 6-dichlorophenolindophenol. Under the proposed conditions the resulting solution has a reducing power which is equal to 0·25 mgrm. of ascorbic acid per ml. of reaction mixture, and which may be used for the standardisation of the indicator solutions when ascorbic acid is not available. The experimental procedure used to obtain the solution of the glucoreductone and proposed as standard is as follows:—Five ml. of a 0·5 per cent. solution of Bureau of Standards glucose are placed in a test-tube, followed by 0·5 ml. of 0·5 *N* sodium hydroxide solution, and the tube is closed by a Bunsen valve. The test-tube is immersed in a water-bath at 80° C. for exactly 12 minutes, then cooled, and 1 ml. of 10 per cent. hydrochloric acid is added, making a total volume of 6·5 ml. This reaction mixture is used immediately for titrating a small amount (0·1 to 0·5 ml.) of the indicator solution from a micro-burette according to the modification by Birch, Harris and Ray (*Biochem. J.*, 1933, **27**, 590) of Tillmans' method. After the pink colour disappears the solution is divided into two equal parts, and to one part one more drop of the reaction mixture is added to ensure that the titration has been completed; even with fresh indicator solutions the colour often becomes brownish, but does not change further when more reductone solution is added, and so must be regarded as the end-point. It is shown that the reducing power of the reaction mixture is almost constant between 12 and 15 minutes of heating. Longer heating always lowered the reductone-content of the mixtures, probably owing to further decomposition of the reductone by the alkali. To obtain the value for the ascorbic acid equivalent of the reductone solution a number of 5-ml. samples, taken from different 0·5 per cent. glucose solutions, were used. Calculated for 1 ml. of the indicator solution, they required an average of 2·12 ml. of the heated reaction mixture. The indicator was titrated with a freshly-made 0·1 per cent. ascorbic acid solution. It was found that 2·12 ml. of the reaction mixture and 1 ml. of the indicator were equal to 0·54 mgrm. of ascorbic acid; therefore, 1 ml. of the heated reaction mixture ≡ 0·25 mgrm. of ascorbic acid. P. H. P.

Vitamin-Content of Cod-Liver Oil as influenced by the Nutritional State of the Cod. E. Poulsson and F. Ender. (*Amer. J. Pharm.*, 1934, **106**, 102–106; *Skand. Archiv für Physiol.*)—In Newfoundland the cod fisheries work from July to September, when the spawning is finished, and the cod are well fed and plump, with large livers containing 50 per cent. or more of oil. On the west coast of Norway, however, the fishery operates during the spawning season from January to April, and, as large numbers of fish are taken over a relatively small area and food becomes scarce, the fat stored in the body and in the liver is drawn upon for nourishment. As the fish become leaner, the liver shrinks, and its proportion of fat diminishes. The authors have examined 43 samples of Newfoundland oils and 95 of Norwegian oils for vitamins *A* and *D*. The vitamin *A* was determined by the Carr–Price colour reaction, and vitamin *D* by experiments on rats. The results show that liver-oil from spawning, ill-nourished cod contains a somewhat smaller amount of vitamin *A*, but considerably more vitamin *D* than the liver-oil from well-nourished, non-spawning fish. As vitamin *A* is necessary for the maintenance of the body, even with adult fish, the stores are consumed when the supply of food becomes scarce. On the other hand, vitamin *D* is not consumed by the mature fish, the skeleton of which is completely developed, so that the proportion of this vitamin in the diminished quantity of oil increases. T. H. P.

Histochemical Detection of Iron and Zinc in Citrus Leaves. H. S. Reed and J. Dufrenoy. (*Compt. rend.*, 1934, **198**, 1535.)—Leaves of citrus plants affected with mottle, and green leaves from plants that had been rendered immune by treatment of the roots, 20 months previously, with zinc sulphate, were fixed in a mixture of 95 parts of alcohol and 100 parts of formaldehyde, and embedded in paraffin wax. Microtome sections, 6μ thick, were cut, and submitted to micro-incineration so as to leave an ash retaining its histological structure. The ferrocyanide reaction showed the presence of iron in the area around the starch grains, even in leaves deficient in chlorophyll and affected with "mottle." If the ash of a section is treated with sodium nitroprusside (Bradley), crystals of zinc nitroprusside are revealed in abundance in each vacuole enclosing a crystal of calcium oxalate in the leaves from plants grown in soil that had been treated with zinc sulphate. The zinc appears to play a part in the oxidation-reduction equilibrium of the plant. Photomicrographs are given. R. F. I.

Organic Analysis

Volumetric Determination of Formaldehyde in the Presence of Sulphites. J. Eury. (*J. Pharm. Chim.*, 1934, **126**, 261–264.)—Since the double sulphite of mercury and sodium in alkaline solution is reducible by formaldehyde, the formaldehyde originally present may be volumetrically determined. Fifty ml. of a 10 per cent. solution of sodium sulphite (to which 1 per cent. of sodium citrate has been added to retard oxidation), 15 ml. of sodium hydroxide solution, and 50 ml. of a mercuric chloride solution containing 278 grms. per litre are placed in a 250-ml. flask, and sufficient of the sample is added to introduce about 0·08 to 0·1 grm. of formaldehyde. The solution is allowed to stand for 15 minutes, with occasional shaking, and is made up to 250 ml.; after standing for 15 to 20 minutes, the mercury is deposited. The liquid is filtered, and the mercury in 100 ml. is determined by the author's modification of the Denigès method (*Bull. Soc. Pharmacol.*, 1930, **37**, 599). From this is deduced the quantity of mercury consumed, and thus the proportion of formaldehyde present, 200 parts of mercury being taken as equivalent to 30 of formaldehyde. D. G. H.

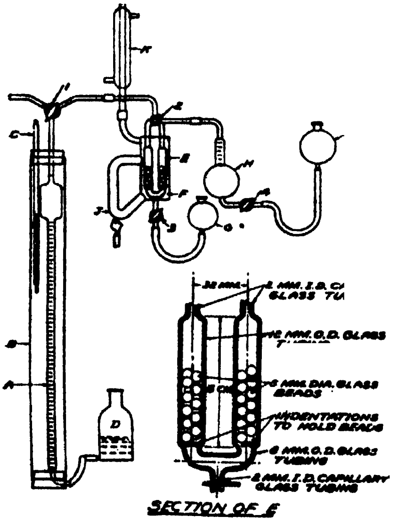
New Method for the Determination of Acetyl Values of Lipids, Applicable to Hydroxylated Fatty Acids. E. S. West, C. L. Hoagland and G. H. Curtis. (*J. Biol. Chem.*, 1934, **104**, 627–634.)—A new modification of Verley and Bolsing's method of acetylation (*Ber.*, 1901, **34**, 3354, 3359; *cf.* Peterson and West, ANALYST, 1927, **52**, Abst., 607; and Marks and Morrell, ANALYST, 1931, **56**, 428) is described, in which the hydroxylated substance is treated, hot or cold, with a measured quantity of a mixture of acetic anhydride and pyridine (one volume of anhydride and 7 volumes of pyridine), the excess of anhydride is decomposed with hot water, and the acidity is titrated with standard alcoholic soda after addition of sufficient butyl alcohol to form a homogeneous solution. Acetylation is carried out in stoppered flasks, the stoppers being moistened with pyridine. A new definition of the acetyl value more suitable for calculation is proposed, *viz.* the acetyl value equals the number of mgrms. of acetyl taken up per grm. of substance. The value is found by means of the formula—acetyl value $= (E \times 4{\cdot}3)/A$, where E represents the ml. of $N/10$ alkali equivalent to anhydride bound, and A the weight of substance acetylated. P. H. P.

Use of Methoxyacetic Anhydride for the Determination of Hydroxyl Groups. D. W. Hill. (*J. Amer. Chem. Soc.*, 1934, **56**, 993.)—An advantage is claimed for methoxyacetic anhydride over acetic anhydride in the determination of hydroxyl groups, since for the methoxyacetyl derivative formed the methoxyl value may be determined, a procedure which is considered more satisfactory on a micro-scale than the determination of the acetyl value after acetylation. A number of methoxyacetyl compounds have been prepared with the aid of methoxyacetic anhydride by methods similar to acetylation with acetic anhydride.

S. G. C.

Determination of Furfural with Bromine. E. E. Hughes and S. F. Acree. (*Ind. Eng. Chem., Anal. Ed.*, 1934, **6**, 123–124.)—At a temperature of 0° C., furfural in dilute hydrochloric acid solution has been found to react quantitatively with 1 molecular proportion of bromine within about 3 to 10 minutes, without any further reactions such as occur as at the ordinary temperature. The furfural solution in 3 per cent. hydrochloric acid is placed in a stoppered flask carrying two side arms, to hold measured volumes of 0·1 *N* potassium bromate solution and 10 per cent. potassium iodide solution, respectively. The flask and contents are cooled to 0° to 2° C. in an ice- and water-bath. The reaction is started by tilting the flask to allow the measured excess of bromate solution to run into the furfural. After 5 minutes, 10 ml. of potassium iodide solution in the other side arm are run into the mixture. The flask is removed from the ice-bath, shaken vigorously to allow the enclosed bromine vapour in the flask to react with the potassium iodide, and the solution is titrated with 0·1 *N* thiosulphate solution, with starch as indicator; 1 ml. of 0·1 *N* potassium bromate solution ≡ 0·0048 grm. of furfural.

S. G. C.



Determination of Butadiene in Gases. H. Tropsch and W. J. Mattox. (*Ind. Eng. Chem., Anal. Ed.*, 1934, **6**, 104–106.)—A method is proposed for the determination of butadiene in gas mixtures in which molten maleic anhydride is employed as absorbent. From 2 to 2·5 grms. of freshly-distilled maleic anhydride are heated to approximately 100° C. and drawn into the heated absorber E (Fig. 1) through stopcock 3. The rubber connection to *G* is replaced, and mercury is introduced into *E* until all gas is displaced and the molten anhydride stands in the capillaries just above the top of jacket *F*. By means of mercury from *I*, all gas is displaced from *H* and the capillary connection to *E*. A 100-ml. portion of the gas to be analysed is taken into the burette, the mercury level in *E* is lowered to the bottom of the U-tube, and the gas is passed from *A*, through *E*, into bulb *H*, the rate of passage being regulated by adjusting stopcock 4. The gas is then passed back into *A*, through *E*, by lowering the levelling bottle *D* and raising *I*. The gas remaining in *E* is displaced by raising the molten maleic anhydride into the capillaries just below stopcock 2. The volume is then read, and the operation is repeated, once or twice, until no further absorption is observed, the temperature of *E* being kept at 100° C. A preliminary run with a portion of the gas to be analysed should be made in order to saturate the maleic anhydride physically with any hydrocarbons which may be present in the mixture. Olefines are without interference; acetylene may be present without effect in concentration up to 15 per cent. S. G. C.

Wax-content and Feel of Indian Cottons. N. Ahmad and D. L. Sen. (*J. Text. Inst.*, 1934, **25**, 150T.)—The wax-content of 12 Indian cottons varied from 0·229 to 0·544 per cent. on the dry cotton. The feel varied from rough in those of low wax-content to silky in those of higher wax-content. For the determination of the wax, 2·5 grms. of the clean cotton of known moisture-content are extracted in a Soxhlet apparatus with benzene for 4 hours. The extract is filtered hot into a tared weighing bottle and evaporated at 90° C., and the residue is heated to constant weight at 100° C. Ether is too volatile to use in Indian laboratories.

R. F. I.

Colour Reactions of Metadinitrobenzene in Alkaline Medium. Determination of Benzene Vapour in the Air. M. Péronnet and R. Truhaut. (*Bull. Soc. Chim.*, 1933, **53–54**, 1464–1474.)—A study of the colour reactions of *m*-dinitrobenzene in alkaline medium has shown that certain aldehydes which give no colour reaction in the cold, give one on heating; that uric acid alone among the purine bases examined gives a colour reaction, and this may be used to identify the acid; further, that creatinine may be distinguished from creatine, since the former gives a positive reaction and the latter none. Certain amino acids give a violet ring with the reagent if 2 ml. of a 10 per cent. alcoholic solution of *m*-dinitrobenzene are superimposed, without mixing, on a solution of 0·1 grm. of the acid in 2 ml. of a 10 per cent. sodium hydroxide solution. Phenyl-β-alanine gives an intense violet colour, but phenyl-α-alanine gives no colour under these conditions.

The determination of benzene vapour in air is based on the transformation of the benzene into the metadinitro derivative by the action of a mixture of concentrated sulphuric acid and fuming nitric acid at a low temperature, and by the colour reaction given by the *m*-dinitrobenzene in alcoholic and alkaline solution with the reducing sugar laevulose. A double bubbler is connected at one end with an aspirating flask, and at the other with a flask which is fitted with a funnel, and into which is introduced, in a small ampoule, a given weight of benzene (10 to 60 mgrms.). The stopcocks are closed, the ampoule is broken, and slight heat is applied to vaporise the benzene. The vapour in the flask is subsequently displaced, with the aid of aspiration, by mercury introduced through the funnel. The first bubbler contains 2 ml. of the sulphuric-nitric acid mixture, and the second, which serves as a guide to total absorption in the first, contains 1 ml. of the same mixture. The benzene is usually all retained in the first bubbler. At the end of the reaction the bubblers are immersed in a sodium chloride freezing mixture and left for 1 hour, after which 5 ml. of water are added, drop by drop. This, incidentally, washes the glass connections, and 14·2 + 4 ml. (under the above conditions) of 25 per cent. sodium hydroxide solution are then added, 12·2 ml. for the first bubbler, and 6 ml. for the second. After being emptied, the bubblers are washed out several times with 25 ml. of 95 per cent. alcohol. The clear liquid is decanted, the precipitate is washed with 70 per cent. alcohol, and the liquid and washings are made up to 100 ml. The alkalinity should be 0·125 *N*, and between 25 and 125 mgrms. of *m*-dinitrobenzene should be present. To 10 ml. of the liquid are added 10 ml. of a 1:200 solution of laevulose in 70 per cent. alcohol, the mixture is rapidly filtered, and the filtrate is held at 25° C. for 20 minutes. A comparative test is made at the same time with a known quantity of benzene and with 3 ml. of the sulpho-nitric mixture. It is found that the intensity of the violet colour superimposed on the yellow (which cannot be quite eliminated, even when working at a low temperature) is proportional, when compared in a colorimeter, to the quantity of benzene present. D. G. H.

Detection of Small Amounts of Pyridine, particularly in Burnt Wood. A. Brüning and M. Schnetka. (*Chem.-Ztg.*, 1934, **58**, 156–157.)—For solutions over 1:1000 in strength, precipitating agents (*e.g.* tannin, picric acid, Nessler's reagent or potassium ferrocyanide) may be used. Cadmium chloride is unsuitable on account of the time required to produce its characteristic precipitate, but potassium iodide, bromine water and mercuric chloride act more rapidly. For dilutions of 1:10,000 use may be made of the crystalline precipitate produced with gold chloride or of the violet colour produced by 1-chloro-2.4-dinitrobenzene in the presence of alkali. For dilutions of 1 : 100,000 the cyanogen bromide reaction of Goris and Larsonneau (*Bull. Sci. Pharmacol.*, 1921, **28**, 497) has been suggested, the reagent being prepared (after C. Göpner, *Z. angew. Chem.*, 1901, 355) by adding 1·6 ml. of sulphuric acid (sp.gr. 1·84) to a solution containing 2 grms. of sodium bromide and 1·5 grm. each of sodium bromate and sodium cyanide in 70 ml. of water. This reagent, which decreases in sensitiveness after 1 week, is added to the pyridine solution together with 1 drop of aniline, when a red precipitate is produced in dilutions of 1 : 100,000, and a red colour in dilutions of 1 : 1,000,000. The colour is due to the bromide of α-anilido-*N*-phenyl-dihydro-pyridine (*cf.* W. König, *ibid.*, 1905, p. 115, and *J. prakt. Chem.*, 1904, pp. 69, 105, who showed that various colours were obtainable by varying the nature of the nitrogen compound used). Tests on the steam-distillates from the extracts in water of the residues from woods which had been soaked with pure alcohol or distilled spirit and ignited, indicated that furfuraldehyde also gives the Goris-Larsonneau reaction, the presence of this substance in such distillates being confirmed by the reaction with aniline and acetic acid. In both reactions the intensity of the red colour depends on the p_H value, and is increased by the presence of an excess of aniline in the former case, but decreased in the latter. Other substances which occur in wood-tar (*e.g.* alcohols, aldehydes, ketones, organic acids, phenol, guaiacol, pine wood oil) gave no colour which might be confused with that given by furfuraldehyde and pyridine in the cyanogen bromide reaction, and numerous other organic substances present did not interfere; the tobacco alkaloids (nicotine, nor-nicotine and 2-β-pyridyl piperidine), α- and β-picoline, the steam distillates from pyroligneous acid, pix liquida and oleum rusci gave strongly-positive reactions. A selective reaction for pyridine, in the presence of furfuraldehyde is as follows:—In 5 ml. of a neutral or weakly-acid solution of the sample are dissolved 1 to 2 grms. of solid sodium acetate (to serve as a buffer), and then 0·5 ml. of the above cyanogen bromide reagent and 1 ml. of a saturated aqueous solution of benzidine are added. After 1 minute at room-temperature, a carmine-red colour develops in the presence of α- or β-picoline or of 1 part in 10,000 to 1,000,000 of nicotine or pyridine; wood tar, tobacco smoke and roasted coffee also gave a positive reaction, but no pyridine was indicated in the steam-distillate obtained after extracting wood from burnt conifers. The amount of air present during combustion is probably an important factor in determining the presence of pyridine, since when various nitrogenous substances (*e.g.* leather, flesh, etc.) and various woods were heated in a retort, pyridine was detectable in the distillate, whilst the steam distillate obtained from the residue when ignition occurred in the open air gave a negative reaction.

J. G.

Inorganic Analysis

Colorimetric Determination of Lead. S. Feinberg. (*Z. anal. Chem.*, 1934, 96, 415–418.)—The lead is converted into molybdate, and the molybdenum is determined colorimetrically with thiocyanate after reduction with stannous chloride. The lead (0·1 to 1·7 mgrm.) is conveniently obtained by anodic deposition. The anode is treated, drop by drop, with hot hydrochloric acid, the solution is diluted to 40 ml., neutralised with ammonia, acidified with 15 to 20 drops of acetic acid, and treated, while boiling, with 10 to 15 ml. of 0·5 per cent. ammonium molybdate solution. When coagulated after some minutes' boiling, the precipitate is collected on a small pad of filter pulp, and washed with water containing a little acetic acid. The pad is then washed 7 or 8 times with 5-ml. portions of 10 per cent. sulphuric acid, the cold solution being treated first with 10 ml. of 5 per cent. potassium thiocyanate solution and stirred, then with 5 ml. of 10 per cent. stannous chloride solution in hydrochloric acid (1 : 4), and, finally, diluted to 100 ml. with 10 per cent. sulphuric acid. The orange-yellow colour is matched against that of a standard molybdenum solution (0·2 to 0·25 grm. MoO_3 in 10 ml. of 1 : 1 sulphuric acid, and diluted to 500 ml.). The molybdenum-content of the quantity of standard solution taken should closely approximate that of the unknown solution, but should not be higher; the standard solution is run into 50 to 60 ml. of 10 per cent. sulphuric acid contained in a colorimeter cylinder, thiocyanate and stannous chloride being added in order. If the colour of the standard solution is slightly weaker than that of the unknown a few drops of the molybdenum solution may be added to the former. W. R. S.

Glycerin as a Reagent for Mercury. M. Stschigol. (*Z. anal. Chem.*, 1934, 96, 328–333.)—Glycerin reduces alkaline mercury solutions, the metal being precipitated. The solid substance or the solution is shaken with 10 per cent. potassium iodide solution, treated with 30 per cent. caustic soda solution, and filtered. The filtered solution is treated with a little more alkali, and boiled for some minutes after addition of 1 ml. of glycerin. The presence of mercury is indicated by a black precipitate or the darkening of the liquid. For quantitative purposes, 0·2 to 0·4 grm. of the material is dissolved in water or a suitable acid, and the solution is boiled with 20 to 30 ml. of 30 per cent. alkali and 5 to 10 ml. of glycerin for 5 minutes.

The addition of glass beads is recommended. The liquid is diluted to about 100 ml. and filtered through a double paper. The precipitate is washed with water until free from chloride and alkali, and dissolved in 10 to 15 ml. of hot nitric acid (sp.gr. 1·4). The solution is diluted with 50 ml. of water and treated with permanganate until faintly pink, and the tinge is just removed with ferrous sulphate. The cold solution is titrated with 0·1 *N* ammonium thiocyanate solution in presence of ferric alum; 1 ml. is equivalent to 0·01003 grm. of mercury. W. R. S.

Determination of Mercury in Galenicals, and its Separation from Bismuth. E. Schulek and S. Floderer. (*Z. anal. Chem.*, 1934, **96**, 388–398.)—The material is dissolved in, or extracted with, 5 per cent. hydrochloric acid; addition of a little bromine water is necessary for calomel. Mercury is extracted from ointments by solution in chloroform and agitation with dilute hydrochloric acid; gelatin preparations are hydrolysed by boiling with hydrochloric acid (reflux condenser). Organic mercury compounds and preparations containing vegetable substances are destroyed by strong sulphuric acid and hydrogen peroxide in a distillation flask connected with a receiver, to avoid loss of mercury if chlorine is present. The mercury solution is precipitated with hydrogen sulphide, and the precipitate is dissolved in sulphuric acid and hydrogen peroxide; the mercury is then titrated by Volhard's thiocyanate method. Bismuth does not interfere in the titration, which may be carried out in sulphate or nitrate solution; halogen, cyanide, and cyanate interfere. If a determination of bismuth is also required, a separation is achieved by means of hydrogen sulphide in a solution containing 20 per cent. of hydrochloric acid; less than 4 per cent. of bismuth should be present. The mercury precipitate is washed free from bismuth with the 20 per cent. acid, preferably by centrifuging and decanting. The washed precipitate, which contains combined chlorine, is dissolved in a little bromine water, the excess of bromine is removed with hydrazine, and the mercury is once more precipitated as sulphide, this time in an easily filterable form free from chlorine. W. R. S.

Gravimetric Determination of Copper, Cadmium, and Nickel as Complex Mercury Compounds. A. Taurins. (*Z. anal. Chem.*, 1934, **97**, 27–36.)—Methods are described for the precipitation of $[Cu(NH_3)_4]\,[HgI_3]_2$ with 4·912 per cent. Cu, of $[Cd(NH_3)_4]\,[HgI_3]_2$ with 8·375 per cent. Cd, and of $[Ni(NH_3)_6]\,[HgI_3]_2$ with 4·434 per cent. Ni, from ammoniacal solutions by means of mercuric potassium iodide. The precipitates are collected on a porous crucible, washed with alcohol and then with ether, and weighed after being dried *in vacuo*. Nickel may thus be separated from cobalt, after oxidation of the latter in ammoniacal solution by means of hydrogen peroxide. Full details are given in the original. W. R. S.

Volumetric Determination of Tin with Potassium Iodate. J. B. Ramsay and J. G. Blann. (*J. Amer. Chem. Soc.*, 1934, **56**, 815–818.)—Stannous tin in dilute hydrochloric acid solution under an atmosphere of carbon dioxide may be determined by titration with standard potassium iodate solution, a slight excess of iodate being added, as shown by the liberation of iodine, which is back-titrated with standard thiosulphate solution, with starch as indicator. The most suitable concentration of acid is 1 *N*, a slight negative error being produced in more strongly acid liquid. In connection with the reduction of stannic tin to the stannous state by the aid of zinc, it was found that the tin sponge would re-dissolve more rapidly if a little cobalt or nickel chloride had been added to the solution, an effect which is considered to be due to co-precipitation of cathodic particles of cobalt or nickel. S. G. C.

Benzoate Method for the Precipitation of Iron, Aluminium and Chromium. I. M. Kolthoff, V. A. Stenger and B. Moscovitz. (*J. Amer. Chem. Soc.*, 1934, **56**, 812–815.)—The precipitation of the hydroxides of the iron group in the presence of ammonium benzoate is claimed to yield a precipitate more readily filterable and less liable to occlude other ions than usual. The procedure is to add ammonia to the slightly acid solution until the precipitate formed redissolves very slowly; 1 ml. of glacial acetic acid and sufficient ammonium chloride to yield about 1 per cent. concentration are added, and about 20 ml. of ammonium benzoate solution (10 per cent.) for every 65 mgrms. of aluminium, or 125 mgrms. of iron or chromium present, are added, with stirring. The suspension produced is boiled gently for 5 minutes, or for 20 minutes if chromium predominates. The precipitate is filtered off on a coarse filter-paper, and washed ten times with hot water containing 1 per cent. of ammonium benzoate and 2 per cent. of glacial acetic acid, to prevent peptisation. For exact work, the filtrate and washings should be evaporated to about 50 ml. for the recovery of incompletely precipitated iron or chromium. The results of test experiments showed that the co-precipitation of zinc, manganese, cobalt, nickel and calcium was slight but definite, particularly in the presence of much tervalent metal. Under the conditions employed, partial precipitation of, *e.g.* lead and copper, occurs in the absence of hydroxides of the iron group. S. G. C.

Determination of Manganese with Anthranilic Acid. H. Funk and M. Demmel. (*Z. anal. Chem.*, 1934, **96**, 385–388.)—Manganous anthranilate (16·80 per cent. Mn) is white and crystalline, and a little more soluble than the metallic compounds previously described (ANALYST, 1933, **58**, 241, 567). Hence the precipitation is carried out in small bulk and with a large excess of sodium anthranilate. The neutral solution (0·1 grm. Mn, 80 ml.) is treated with 60 ml. of 3 per cent. reagent. The precipitate is collected, after one hour's standing, in a porous crucible, and washed with 0·5 per cent. reagent and then with alcohol, and dried at 105° to 110° C. The bromimetric titration of the precipitate may be carried out as already shown (ANALYST, 1933, **58**, 361). W. R. S.

Colour Reactions of Rhenium. B. Tougarinoff. (*Bull. Soc. Chim. Belg.*, 1934, **43**, 111–114.)—Ferrocyanide and dimethylglyoxime give characteristic colours in presence of stannous chloride. The ferrocyanide test is carried out as follows:—One ml. of neutral or acid perrhenate solution is treated with a few drops of 5 per cent. potassium ferrocyanide solution and 2 to 3 ml. of stannous chloride reagent (25 grms. of salt in 100 ml. of strong hydrochloric acid). The resulting colour is pale brown to red-brown. The addition of water produces a purple colour, which permits of the identification of 0·01 mgrm. of rhenium. Sulphate does not interfere, but nitrate in concentration above 0·5 N does. The following elements mask the reaction: nickel, cobalt, chromium, tungsten, vanadium, and niobium; hence, rhenium must be separated from them by distillation with strong sulphuric acid at 190° C. (thermometer in liquid) in a brisk current of air. The distillate is received in a solution containing ferrocyanide and stannous chloride, a rose-red colour after 15 to 20 minutes' distillation indicating rhenium. Molybdate solutions give a golden-yellow precipitate if free from rhenium; a small admixture of that metal causes the precipitate to turn brownish-yellow. For the dimethylglyoxime test, 1 ml. of perrhenate solution is treated with a few drops of the alcoholic solution of the reagent, and stannous chloride as before. The resulting colour is yellow to deep red, according to the quantity present. The yellow colour turns green on warming; the deep-red solution assumes a green fluorescence under those conditions. It is possible thus to identify 0·01 mgrm. of rhenium in the presence of several other metals; if a precipitate forms, it is separated from the warmed liquid by filtration; a green filtrate indicates the presence of rhenium.

W. R. S.

Analytical Reactions of Rubidium and Caesium. W. J. O'Leary and J. Papish. (*Ind. Eng. Chem., Anal. Ed.*, 1934, 6, 107–111.)—The analytical literature on rubidium and caesium is critically reviewed. Caesium and rubidium may be quantitatively precipitated and separated almost completely from potassium by the addition of luteophosphomolybdic acid (9-phosphomolybdic acid, Kehrmann and Böhm, *Z. anorg. Chem.*, 1894, 7, 406), which is prepared by heating the commercial dodeca-phosphomolybdic acid at 300° to 350°C. until it changes in colour from orange to green, and then extracting and crystallising the solution of the green material. The caesium and rubidium precipitates were of somewhat indefinite composition; they were therefore converted into chloroplatinates after removal of the molybdenum as sulphide. Recovery of upwards of 99 per cent. of the rare alkali metals (calculated as chlorides) was thus obtained from mixtures with up to 100 parts of potassium nitrate. Modifications of the silicotungstate and chloroplatinate methods are described. S. G. C.

Applications of Chloramine in Volumetric Analysis. A. S. Komarowsky, W. F. Filonowa, and I. M. Korenman. (*Z. anal. Chem.*, 1934, 96, 321–328.)—Chloramine (sodium *p*-toluenesulphochloramine, $CH_3.C_6H_4.SO_2NNaCl$) is a cheap substitute for iodine (*cf.* ANALYST, 1927, 52, 668). The authors have applied it to the determination of ferrocyanide, thiocyanate, hydrazine, hypophosphite, and carbon disulphide. The solution used (15 grms. per litre, which is nearly 0·1 *N*) was standardised against arsenious oxide in presence of starch and very little potassium iodide, as well as against an acidified solution of potassium iodide, the liberated iodine being titrated with thiosulphate.

Ferrocyanide.—The titration must be carried out in weakly acid, not in neutral or alkaline solution. The ferrocyanide (about 0·4 grm.) is dissolved in 100 ml. of water, in a glass-stoppered flask, and the solution is treated at 40° C. with 5 ml. of 0·5 *N* hydrochloric acid and 20 ml. of chloramine solution. The excess of the latter is then ascertained by addition of 0·8 grm. of sodium bicarbonate and a known excess of arsenite solution, which is titrated with chloramine after addition of starch and a crystal of potassium iodide.

Thiocyanate.—The solution (100 to 150 ml.) is treated with 2 grms. of bicarbonate and 50 ml. of chloramine solution, and left in the dark for 4 hours at ordinary temperature. The excess of reagent is then determined by addition of 20 ml. of 2 *N* hydrochloric acid and 1 to 2 grms. of potassium iodide, with subsequent thiosulphate titration; or by arsenite in excess, which is titrated by chloramine in presence of starch and a crystal of iodide.

Hydrazine.—A 0·1 *N* solution (10 ml.) is treated with 0·5 grm. of bicarbonate in 15 ml. of water, a crystal of iodide, and starch solution, and titrated slowly with chloramine, with constant stirring.

Hypophosphite.—The results are serviceable, but slightly lower than by iodimetric titration. A solution of calcium hypophosphite (1 grm. in 250 ml. of water) is treated with 10 ml. of sulphuric acid (1 : 5) and 30 ml. of chloramine solution. After 24 hours, 2 grms. of potassium iodide are added, and the iodine is titrated with thiosulphate.

Carbon Disulphide.—This is dissolved in 5 per cent. alcoholic potash. The solution is made just acid with acetic acid, treated with sodium bicarbonate, and titrated with chloramine after the usual addition of a little iodide and starch. Kept in the dark, the chloramine solution was found to maintain its titre for 40 days.

W. R. S.

Determination of Fluorides in Natural Waters. J. M. Sanchis. (*Ind. Eng. Chem., Anal. Ed.*, 1934, **6**, 134–135.)—In connection with the question of the mottling of tooth enamel caused by the presence of fluoride in drinking water, the following modification of the zirconium–alizarin method has been adopted for the determination of the fluoride: To 100 ml. of the water, filtered, if necessary, and to the prepared standards noted below, are added 2 ml. of 3 *N* hydrochloric acid, 2 ml. of 3 *N* sulphuric acid and 2 ml. of indicator solution (prepared by mixing equal volumes of a 0·17 per cent. solution of sodium alizarin sulphonate and a 0·87 per cent. solution of zirconium nitrate crystals as a stock solution, and diluting 20 ml. of this to 100 ml. as required). The solutions are brought rapidly to the boiling-point and then cooled. Four hours after cooling, or on the following day, the colour of the sample solution is compared with those of the standards in Nessler tubes. The use of a range of nine standards is suggested, *viz.* 0, 2·5, 5·0, 7·5, 10, 15, 20, 25, and 30 ml. of standard sodium fluoride solution (1 ml. ≡ 0·01 mgrm. of fluorine) made up to 100 ml. with distilled water. A slight reddish precipitate, due to appreciable quantities of organic matter or phosphate, which may appear in the solution after cooling, should be dispersed prior to the colorimetric comparison, but in extreme cases, where the amount of precipitate is sufficient to prevent satisfactory comparison, the method of Willard and Winter (*Ind. Eng. Chem., Anal. Ed.*, 1933, **5**, 7), or its modification by Boruff and Abbott (*id.*, 1933, **5**, 236), should be employed. The following have been found not to interfere: chloride, sulphate, bicarbonate, sodium, calcium, and magnesium up to 500 parts per million; manganese up to 200 parts per million; silicate up to 50 parts per million; phosphate, boron, copper, and iron up to 5 parts per million; sulphide up to 2 parts per million. Samples of natural waters from 11 sources in the Los Angeles district gave results from 0·3 to 2·1 parts per million of fluorine.

S. G. C.

Microchemical

Collected References. Detection and Determination of Small Amounts of Cholesterol and other Sterols. A. Wasitzky. (*Mikrochem.*, 1934, **14**, 289–310.)—Most of the methods are described briefly, and some more important methods in detail. Ten references are given on methods of detection of cholesterol. The quantitative methods are divided into:—(i) Colorimetric (46 references); (ii) spectrometric (6 references); (iii) nephelometric (1 reference); (iv) gravimetric (10 references); (v) volumetric (16 references); (vi) other methods (6 references).

J. W. B.

Micro-Determination of Iodine and a Useful Micro-Desiccator. W. Münster. (*Mikrochem.*, 1933, **14**, 23–26.)—The Pregl method of iodine determination is modified by utilising Vieböck and Brecher's titration method (*Ber.*, 1930, **63**, 3207) for the determination of methoxyl, to replace the weighing of silver iodide as the final stage of the determination. The Pregl combustion tube, containing a glass spiral, is replaced by an ordinary micro-combustion tube, 50 cm. in length, and 0·7–0·8 cm. in diameter. One end is attached to a narrow tube, about 0·2 cm. diameter, and 18 cm. long, bent down at right angles to the combustion tube. A small bulb of the same diameter as the combustion tube may be blown in the tube just before the right angle bend, but, although this is useful in preventing any sucking-back of the absorption liquid, it is not indispensable. This narrow outlet tube dips into the absorption liquid in a drawn-out test-tube, in the way used in the methoxyl determination. The combustion is carried out in the usual way in a stream of washed oxygen at the rate of 8 bubbles in 10 seconds; this passes over the substance which has been weighed into a platinum boat and introduced into the combustion tube. The vapours pass over the heated platinum contacts, and are finally absorbed in 2 to 3 ml. of a solution of bromine in acetic acid, as used by Vieböck and Brecher (*loc. cit.*). The combustion is complete in 10 minutes, after which the apparatus is allowed to cool in a stream of oxygen. Finally, the absorption apparatus is washed, and the liquid is transferred to a conical flask containing a few ml. of sodium acetate solution, and, after destruction of the bromine, the iodate is titrated against *N*/100 thiosulphate solution. A complete analysis may be carried out in less than 1 hour. Very good results are obtained from substances with high iodine-content.

A useful micro-desiccator for vacua higher than the Pregl type is made in three parts, attached by ground-glass joints:—(i) A bulb (about 50 ml. capacity) containing phosphorus pentoxide; (ii) a tubular portion which fits in the Pregl drying block contains the boat and substance; (iii) a glass tap which connects with the suction-pump through a tube containing calcium chloride. J. W. B.

Micro-Determination of Silica in Tissues and in Blood. G. Rodillon. (*Bull. Biol. Pharm.*, 1934, **1**, 33–59.)—This is a modification of Isaacs' method (*Bull. Soc. Chem. Biol.*, 1924, **6**, 157), already modified in different ways by King (*Biochem. J.*, 1933, **27**, 990), and as used by Parri and Scotti (*J. Pharm. Chim.*, 1933, **125**, 513). The method consists in (i) Decomposition of organic matter, by fusing about 0·05 grm. of the dried and powdered tissue with about 8 times its weight of sodium bicarbonate, with, if necessary, the addition of a few small crystals of ammonium nitrate. (ii) Formation of the silico-molybdate, by adding 1 ml. of 10 per cent. ammonium molybdate solution to the solution of the ash in 2 drops of dilute nitric acid and a few drops of 30 per cent. sulphuric acid and heating to 60° C. To prevent the interference of phosphates, 1 ml. of 95 per cent. alcohol is added to the molybdate solution, and, after the addition of the solution of the ash, 1 ml. of a solution of ammonium citrate (2 grms. of citric acid, 10 grms. of water, and 10 ml. of concentrated ammonia) is added. (iii) Reduction of the silico-molybdate, by means of two reducing agents—hyposulphite and hydroxylamine—to give a blue colour. The sodium hyposulphite (0·35 grm.) and hydroxylamine hydrochloride (0·35 grm.) are added to the test-solution and dissolved without heating, and the mixture is diluted to 10 ml. (iv) The blue colour of the solution is compared in a colorimeter, after filtration, if necessary, with that given by a standard solution of silica. J. W. B.

Rhodizonic Acid as an Indicator in the Volumetric Determination of Barium. A. Friedrich and S. Rapoport. (*Mikrochem.*, 1933, **14**, 41–48.) — Rhodizonic acid is unsuitable as an indicator for the determination of barium in acid solutions, as the end-point is dependent on the rate of titration. Unreliable results were also obtained in neutral solution, owing to the fact that the rhodizonate is present as an almost insoluble suspension colloid, and also is inactivated by the precipitated barium sulphate. By the addition of gelatin solutions better results are obtained by titration in neutral solutions, but a comparison with the end-point colour must always be made. Small amounts of barium may be precipitated with sodium rhodizonate in the presence of gelatin, and the barium in the suspension may be determined colorimetrically by means of a Pulfrich photometer. The coloured solution is sensitive to light. J. W. B.

Physical Methods, Apparatus, etc.

Identification of Tanning Agents under the Quartz Mercury-Vapour Lamp. L. Pollak. (*Coll.*, 1933, 628 ; *J. Text. Inst.*, 1934, **25**, A200.)—A fabric is used consisting of wool through which silk and mercerised cotton threads are drawn in the warp direction and rayon and cotton threads in the weft. Pieces of this fabric (5 × 5 cm.) are immersed for 30 minutes in a boiling water-bath in 50 ml. of a solution containing 2 or 4 grms. of the liquid tannin extract per 100 c.c. and 2 ml. of 2 per cent. acetic acid, and then washed and dried. Daylight and filtered ultra-violet light show different effects on the different threads. The characteristics of a variety of extracts are tabulated. In most cases the cellulosic fibres are scarcely tinted, but show a distinctive fluorescence in ultra-violet light, the colour varying with the nature of the tannin extract. R. F. I.

Fading [Tests for Dyes]. J. Grant. (*Proc. Tech. Section, Paper Makers' Assoc.*, 1934, **14**, 335–347.)—Methods of carrying out fading tests, with special reference to dyed and undyed paper, are critically reviewed. Neither the filtered nor unfiltered light from the mercury or carbon arc is completely satisfactory for reproduction of the effect of exposure to daylight, although the latter is preferable, and both give misleading results in some cases. As a standard method it is suggested that typical dyes from each of the basic, acid and direct dyestuff classes should be exposed for total periods of 1, 2 and 3 weeks, respectively, at 20 to 23° C. and 60 per cent. relative humidity, between 10 a.m. and 3 p.m., to a cloudless north sky during June and July, nine such standards being chosen so as to provide for a red, yellow and blue dye in each class. In order to carry out the test, the sample is exposed at any time or place simultaneously with a duplicate of whichever standard it most closely resembles in properties and shade, until it has faded to the same extent as the faded standard; the change in colour so produced in the sample can then be taken as due to reproducible conditions of exposure. As this is slow, especially in the winter, and cannot be used at night, it is further suggested that the change in appearance in filtered ultra-violet light produced by exposure to unfiltered ultra-violet light from the mercury arc should be taken as an indication of the change in appearance in visible light produced by exposure to visible light. A numerical expression of fastness to light may then be obtained from the minimum period required to produce the first change plainly visible to the naked eye, and this may vary from a few minutes for a fugitive dye to many hours for a fast dye. The method is subject to the same limitations as the direct use of ultra-violet rays as a fading agent, but gave reliable indications for about 75 per cent. of the dyes tested. It is very useful for routine tests and for work with dyes the properties of which are known, but may give misleading results in certain cases, *e.g.* when a particularly fast dye or pigment colour is used, and the paper itself changes in appearance first. In all such tests the lamp should be allowed to run for 5 minutes in order to eliminate the effect of the ozone usually produced during this initial period. Applications of the method to various problems of paper technology are described (*cf.* Bromley, ANALYST, 1933, **58**, 29). J. G.

Reviews

HANDBUCH DER LEBENSMITTEL-CHEMIE. Vol. II. ALLGEMEINE UNTERSUCHUNGS-METHODEN. Part I. PHYSIKALISCHE METHODEN. Edited by A. BÖMER. Pp. 536. Berlin: Julius Springer. 1933. Price 66RM. (69RM. bound).

As its title indicates, the second volume of this monumental treatise deals with general processes available for the investigation of foodstuffs, and this part with physical methods. The general scheme of the Handbuch has already been noticed in THE ANALYST (1933, **58**, 503), and the volume now considered continues the same comprehensive thoroughness. Each chapter describes the theory underlying the methods, and their application, giving a description and the mode of use of the various instruments employed. The subjects include specific gravity, viscosity, ultrafiltration, dialysis, surface tension, solubility, melting-point and boiling-point, cryoscopy, calorimetry, p_H, indicators, oxidation-reduction potentials, conductivity, refractometry, spectroscopy, polarimetry, colorimetry, luminescence analysis and microscopy. Chemical and biological methods are promised us in Part II.

The method of treatment seems to be uniformly thorough and, so far as the reviewer can check it, good. There is much to be said for the mode of presentation adopted; suppose one has a melting- or boiling-point to determine on a small quantity of some unusual material, reference to this volume shows at a glance all, or nearly all, the good methods, both macro and micro, so that one can proceed without having to hunt up special journals. Similarly, all the types of instrument for, say, refractive index or viscosity are explained. The method does, however, lead to certain omissions which may perhaps be rectified when we reach volumes dealing with special subjects; thus, there are described several cryoscopes, but not that of Hortvet, which we now all use for our milk samples. Ostwald's, Engler's, and Holde's viscometers are described, but in England Redwood's is the most popular; and tables or formulae connecting the results obtained by these instruments would be useful. The section on quantitative fluorescence analysis is perhaps most novel, and is not usually found in books connected with foods; quinine salicylate, chlorophyll and haematoporphyrin afford examples of its use. Microscopy covers not only matters instrumental, but also section-cutting, staining, photography, histology, and some aspects of bacteriological technique.

The book is concise, encyclopaedic, well written and well produced, and is to be commended, but it costs twice what it should.

H. E. COX

LABORATORY MANUAL OF COLLOID CHEMISTRY. INTRODUCTORY COLLOID CHEMISTRY. By H. N. HOLMES. Pp. xvii+229 and xiv+198, respectively. London: Chapman & Hall. 1934. Price 20s. and 15s. 6d. respectively.

It is a somewhat difficult matter to review each of these books dispassionately, since, in spite of individualised titles, the one is merely a reprint of the other. However, to start with the *Laboratory Manual*: this is a concise, well-written, and amazingly comprehensive book, well calculated to give any reader an insight into the variety and charm of colloid chemistry and to stimulate the desire to know more of the subject. Short and clear directions are given for carrying out numerous experiments, and a running commentary, explaining briefly the background of these, forms a brief but adequate introduction to the theory of the subject.

Besides the experiments, described in detail, there are numerous well-chosen references to descriptions of original work which can be used as a basis for other work. A commendable feature of the book is that the student is encouraged to use his initiative in planning experiments and in deducing the theoretical inferences to be drawn from work he has carried out.

There is a good bibliography of text-books on colloid chemistry, in which the author particularly recommends his own *Introductory Colloid Chemistry* as a helpful introductory manual. While fully endorsing this description, the reviewer cannot help feeling that any student who has bought the *Laboratory Manual* will receive a disagreeable shock when he finds that for fifteen and sixpence laid out in purchasing the *Introductory Colloid Chemistry* about three and sixpence purchases new matter and about twelve shillings merely purchases matter lifted, paragraph by paragraph, and figure by figure, from the *Laboratory Manual*. It is true that the chapters on "Emulsions," "Gels and Jellies: Solvated Colloids," and "Viscosity and Plasticity," have been largely re-written, and that the chapter on "Adsorption from Liquids" contains a reasonable amount of fresh matter. These, however, form only a small proportion of a book in eighteen chapters. It seems a pity that this additional matter was not incorporated in the *Laboratory Manual*, and, considering that the latter is now, deservedly, in its third edition, the publishers could well have done this without raising the price. The *Introductory Colloid Chemistry* need then never have been launched as a separate text-book. The reviewer feels, somewhat strongly, that the student of colloid chemistry may be recommended to buy either of these books—but not both.

D. JORDAN LLOYD

THE ANALYSIS OF OIL FOR PRODUCTION OF LUBRICANTS. ARTHUR A. ASHWORTH, M.A., A.M.I.C.E., M.Inst.P.T. Pp. 63 with 7 plates. London: Ernest Benn, Ltd. 1933. Price 9s. net.

This little book is devoted entirely to one highly specialised process of analysis, *viz.* the estimation of the lubricating oil-content of a crude petroleum or raw stock. It describes clearly and in very great detail the succession of operations involved and various apparatus which have been specially devised for the purpose. The oil after neutralisation is distilled in a pipe-still under a pressure of about 5 to 10 mm. (unless asphaltic matter is absent, when this distillation may be omitted), and chemically refined by treatment with about 5 per cent. sulphuric acid, decantation from the acid tar, and agitation with a decolorising clay and filtration. The filtered oil is then fractionated by distillation from a glass flask under 5-mm. pressure, and from an examination of the viscosities of the fractions, the yield of various lubricating oils, from light spindle oil to heavy cylinder oil, may be calculated.

Such a book, as a whole, can be of interest to only a very limited number of readers, but some of the apparatus described is capable of much more general application, as, for example, a pressure filter, suitable for the filtration of very viscous liquids, which consists of a piece of 3-inch steel pipe, one end of which is closed with a screw cap, through which is inserted an ordinary bicycle tyre valve, whilst at the other end is fitted a disc of fine-meshed copper gauze on to which may be clamped a double thickness of filter-paper. There is also a novel fractionating receiver for collecting a large number of fractions during a vacuum distillation, and a slight modification of the B.E.S.A. U-tube viscometer, better suited to the examination of liquids of high viscosity.

The author is to be congratulated both on the skill with which he has devised the necessary apparatus and on the lucidity with which it is described. There is one small error, however, which might be liable to cause confusion. The unit of kinematic viscosity is throughout the book described as the "poise," whereas it should be the "stoke."

W. H. SIMMONS

ANNUAL REPORTS OF THE SOCIETY OF CHEMICAL INDUSTRY ON THE PROGRESS OF APPLIED CHEMISTRY. 1933. Vol. 18. Price 7s. 6d. to members, 12s. 6d. to others.

If any fault can be urged against the Annual Reports on the Progress of Applied Chemistry, it is that they are too eminently readable. The busy man hurriedly consulting one section is likely to find himself browsing, willy-nilly, in others. To the industrial chemist the book will be a veritable anthology, to be dipped into again and again.

The names of the contributors afford sufficient guarantee that no work of importance has escaped mention. Possibly, a team of literature searchers devoting their full time to the task might discover faults of omission, but certainly in the fields known to the present reviewer the importance of any work passed over is entirely a matter of personal opinion.

Whilst the various reports will be indispensable to specialists, the introductory paragraphs of each might well be read by all who take an intelligent interest in life, whether they be by profession technicians or not, for nowhere are there so readily available equally unbiased and authoritative reviews of the conditions prevailing in modern industry, and the layman, equally with the scientist, could not fail to profit by their perusal. The world depression of the last few years has emphasised how interrelated are all fields of human endeavour, and none, scientist, politician, economist, banker, and business man alike, can afford to ignore the work being done outside his own particular department. All branches of civilisation stand or fall together, so that it is pleasing to note the spirit of optimism which permeates most of these reviews. Even if in 1933 there have been few dramatic and spectacular discoveries to record, this volume shows that, in applied chemistry, as in all other directions, it was a year of steady progress and recovery.

E. W. PATES

EASILY INTERPOLATED TRIGONOMETRIC TABLES WITH NON-INTERPOLATING LOGS, COLOGS, AND ANTILOGS. F. W. JOHNSON, M.A. America: The Simplified Series Publishing Co. Price: From 1 dollar 60 to 4 dollars, according to cover.

The avowed object of this set of tables is to eliminate the operation of interpolation in the use of mathematical tables. This it contrives to do in the case of five-figure logarithms by giving the log for numbers from 10,000 to 99,999, and, in the case of trigonometrical functions, by including a table of proportional parts alongside the one consulted. The tables are also thumb-indexed, so that any appropriate table can readily be found. These features combined should do much to avoid waste of time when the user has become really accustomed to the method of reading the tables, which is novel and, to one more used to the normal form, rather confusing. The author prefers not to use negative characteristics for logarithms, and does this by adding 10 in such cases. This practice and the need for special rules in certain cases call for some mental effort to attain a degree of accuracy in reading compatible with the accuracy of the tables themselves, which are stated to be "always correct to the last figure given."

P. BILHAM

SPIRIT TABLES FOR USE WITH SIKES'S A & B HYDROMETERS. Issued under the Authority of the Commissioners of H.M. Customs and Excise. H.M. Stationery Office, London. 1933. Pp. 68. Price 2s. 6d. net.

The present Tables, legalised by "The Strength and Weight of Spirits Ascertainment Regulations, 1930" (S.R. & O., 1930, No. 328), have been compiled by the late Sir Edward Thorpe and Sir R. Robertson, assisted by members of the Government Laboratory staff. Part I gives directions for the use of Sikes's A and B Hydrometers, followed by two tables, II and V. Table II is for use with the A hydrometer, or B hydrometer with A poise; it covers a temperature range of 30–100° F., by separate degrees, with an extreme range of alcohol strengths, 57·5–75·4 per cent. over proof; at 60° F. the range is 66·7–73·5 per cent. over proof. Table V, for use with the B hydrometer without the poise, covers a temperature range of 47–100° F., with extreme range of alcohol strengths 65·9–75·3 per cent. over proof, at 60° F. the range is 73·5–75·3 per cent. over proof. The wide temperature range obviously renders the instruments serviceable under diverse climatic conditions. Part II gives directions and two tables (IV and VI), for determining the weight, per gallon of spirits, in pounds to three decimal places. Tables IV and VI are to be used with Sikes's hydrometers, as mentioned above, for Tables II and V, respectively. Though no temperature is stated, it is probably assumed that the indications apply to the standard temperature, 60° F.; should the determination be made at another temperature, this must be stated.

This little volume will undoubtedly prove of great service to those who have to deal with high-strength spirits, and praise is due to all who shared in its compilation. Though it seems unfortunate that we still adhere to an arbitrary "Proof spirit" standard, doubtless there are very good reasons for not making a change to a more logical and up-to-date standard.

F. M. CORY

Publications Received

THORPE'S DICTIONARY OF APPLIED CHEMISTRY. Supplement. Vol. I. A to M. Edited by J. F. THORPE and M. A. WHITELEY. Pp. 680. London: Longmans, Green & Co. 1934. Price 60s. net.

ORGANIC CHEMISTRY BY VICTOR VON RICHTER. New Translation by E. N. ALLOTT. Pp. 790. London: Kegan Paul & Co. 1934. Price 35s. net.

ORGANIC SYNTHESES. Vol. XIV. W. W. Hartan, Editor-in-Chief. Pp. 100. London: Chapman & Hall. 1934. Price 10s. 6d. net.

ANNUAL REPORT FOR 1933. Central Narcotics Intelligence Bureau. Egyptian Government. Pp. 168. Cairo. Price P.T. 10.

BIBLIOGRAPHY OF CHLOROPICRIN, 1848–1932. By R. C. ROARK. U.S. Dept. Agriculture. Miscellaneous Publications No. 176. Washington. Price 10 cents.

JULY, 1934 Vol. 59, No. 700

THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

NORTH OF ENGLAND SECTION

THE Fifth Summer Meeting was held at the Craigside Hydro Hotel, Llandudno, from June 22nd to 25th. The attendance was forty-seven, including many ladies.

The Chairman (Professor W. H. Roberts) presided, and among those present were the following:—the President (Mr. John Evans); Past-Presidents (Dr. J. T. Dunn, accompanied by Mrs. Dunn, and Mr. F. W. F. Arnaud with Mrs. Arnaud); Hon. Treasurer (Mr. E. B. Hughes); Editor of the ANALYST (Dr. C. A. Mitchell); Mr. A. L. Bacharach with Mrs. Bacharach, Dr. H. E. Cox, Mr. E. M. Hawkins and Miss Elliott.

On Saturday morning a lecture, illustrated by lantern slides, was given by Professor A. P. Laurie, entitled "Old Masters and Modern Forgeries." Dr. Laurie gave an account of the most recent apparatus and methods, involving the use of infra-red and ultra-violet rays, etc., employed in the examination of pictures. The Vice-Chairman (Mr. A. R. Tankard), who presided in the temporary absence of the Chairman, extended a cordial welcome to the lecturer and to all attending the meeting, especially those from the south. A vote of thanks to Dr. Laurie was proposed by the President and seconded by Mr. Arnaud.

On the motion of Dr. Dunn seconded by Mr. R. W. Sutton, a resolution was unanimously passed, expressing the cordial greetings of the Section and affirming its continued loyalty to the Council of the parent Society.

The meeting received with great pleasure the announcement that the President (Mr. John Evans) was about to receive the degree of M.Sc. (*honoris causa*) from the University of Sheffield and offered him their hearty congratulations.

A telegram was sent to Dr. J. A. Voelcker conveying the hearty congratulations of the Meeting on the attainment of his eightieth birthday.

Mrs. W. H. Roberts presented all the ladies with a Victorian posy and was thanked, on their behalf, by Mrs. J. T. Dunn.

The President proposed a vote of thanks to the Hon. Secretary (Mr. J. R. Stubbs) for his work in arranging the Meeting.

On Sunday afternoon the party proceeded by motor through the Snowdon district to Bettws-y-Coed, where tea was taken.

The Determination of Free Silica in Coal-Measure Rocks

BY A. SHAW, B.SC.

(*Read at the Meeting, May* 2, 1934)

IN silicate rock analysis no great difficulty is experienced in determining the amount of total silica present; to differentiate between the silica present in the free state and that combined as silicates is, however, a problem of much greater difficulty. In the past the problem has been attacked in various ways, but the only method which has met with any degree of success is that evolved by Lunge,[1] Mellor[2] and others, based on the "rational analysis" principle. The method appears to have been used mainly for the determination of free silica in clays, and has met with much adverse criticism on the ground that the results obtained were not in agreement with those calculated from the ultimate analysis. Although neither of these methods was capable of giving results of great accuracy, no further work appears to have been done on the subject. Recently, however, in consequence of the research being carried out on the incidence of silicosis amongst coal miners, it became increasingly important that some reliable means of estimating the free-silica content of rocks and shales should be available; and, with this object in view, investigations were commenced in the Mining Research Laboratory, Birmingham, to compare the various methods in use. Reference to existing literature showed that the methods capable of application to coal-measure rocks were that of calculation from the ultimate analysis, and two modifications of the rational analysis. In addition, Mr. H. V. Thompson, of North Staffordshire Technical College, and Professor Sollas each suggested a method that might be adapted to the determination of free silica in shales. Although neither of these two suggested methods proved capable of general application, a short description of each may be of interest.

THOMPSON'S METHOD.—This is based on the fact that quartz (sp.gr. 2·66) is converted into tridymite (sp. gr. 2·28) when heated under molten sodium chloride for forty-eight hours.[3] The loss on ignition of the sample is first determined, and then the density of the ignited material. After conversion of the quartz into tridymite, the density of the material is again determined. If s_0 and s_1 represent the densities of quartz and tridymite, respectively, d_0 and d_1 the densities of the material before and after conversion of the quartz, and p the percentage loss on ignition, then the amount of quartz present in the original material can be shown to be

$$\frac{(100 - p)\, s_1 s_0 \,(d_0 - d_1)}{d_0 d_1 \,(s_0 - s_1)} \text{ per cent.,}$$

assuming

(i) That, on ignition, none of the quartz becomes combined with the remainder of the material.

(ii) That fusion under molten sodium chloride has no chemical or physical effect on the materials present other than quartz.

(iii) That the free silica is present in the form of quartz with a density approximately 2·66.

Samples of Bedlington shale, Scotch Whinstone, and dust from the Ooregum Mines, Mysore, were subjected to the above treatment, with the result that in each case the sample increased in weight after being heated with molten sodium chloride, showing that combination had taken place. It was concluded, therefore, that the method was not generally applicable, and this conclusion was afterwards confirmed by Thompson, who found that kaolin combined with sodium chloride under the experimental conditions. The residue of quartz, felspar, etc., from the rational analysis of a shale, tested by Thompson's method, gave a result in good agreement with that obtained by correcting for the felspar present in the usual way, showing that the method may be applied in exceptional cases where little or no combination takes place. The tests showed, however, that there was little possibility of the method being successful when applied generally to coal-measure rocks.

SOLLAS'S METHOD.—The method suggested by Professor Sollas consists in the determination of the sp.gr. of the minerals present in the rock and their separation by float and sink tests, the actual procedure being as follows:

The sample is crushed to pass a 30-mesh sieve, washed by sedimentation to remove fine particles and dried, the sp.gr. of the constituent minerals being determined by means of the liquid diffusion column. This is prepared by placing in a long test-tube small amounts of mixtures of bromoform and benzene of varying sp.gr., the heaviest fraction first, and the others in order of decreasing sp.gr. On standing, diffusion takes place until the sp.gr. of the liquid varies fairly uniformly over the length of the tube, *i.e.* the sp.gr. at any point in the liquid is dependent on the depth. The dried sample is introduced into the tube, a little at a time to prevent the grains clogging, and the tube is allowed to stand for a short time. The mineral grains sink until they reach a point where the sp.gr. of the surrounding liquid is equal to that of the grains, and at these points the mineral particles float. By the introduction of various minerals or glass beads of known sp.gr. into the tube, a graph can be drawn showing the sp.gr. of the liquid at any point, and from this and the relative positions of the various bands of particles the sp.gr. of the mineral constituents of the sample can be obtained.

Separation of any particular mineral is then effected by immersion of a fresh portion of sample in a liquid of suitable sp.gr., whereby all heavier minerals are removed. This is followed by a further separation of all light minerals. Although this method has been used successfully by Sollas for the analysis of coarse-grained rocks, it was obvious that greater difficulty would be experienced in its application to the analysis of such fine-grained rocks as coal-measure shales. Moreover, the possibility of the presence, in such shales, of soda-lime felspars having specific gravities approximating to that of quartz would add to the difficulty of effecting a complete separation. In order, however, to obtain information regarding the accuracy of such separation, several tests were made on artificial mixtures of quartz and orthoclase. The results showed that, although good separations could be obtained with mixtures ground to pass a 30-mesh sieve, the error in the case of finer mixtures was of the order of 10 per cent. As shales would have to be ground to pass a 60-mesh sieve, at least, in order to effect any appreciable separation of the mineral grains, it was obvious that the method could not be applied to the separation of quartz from shales.

RATIONAL ANALYSIS.—The two methods suggested by Thompson and Sollas having proved to be inapplicable, attention was then turned to the much-criticised rational analysis. The many variations of this method in existence differ only in experimental procedure, but the principle is the same, *viz.* the attempt to remove from the sample under analysis all minerals except the quartz. The various minerals present are decomposed by suitable treatment with acids (sulphuric and hydrochloric), and the products of decomposition are removed by solution in water and Lunge solution (100 grms. of crystallised sodium carbonate and 10 grms. of sodium hydroxide in 1 litre of solution). Unfortunately, however, the decomposition is seldom complete, with the result that the residue obtained after such treatment contains not only the quartz, but also varying quantities of undecomposed silicates. A correction is usually made for the presence of these undecomposed minerals, by assuming them to be orthoclase, the amount being calculated from the alumina present in the residue. This correction, which is seldom accurate, has given rise to a certain amount of criticism, but, in view of the results obtained from the analysis of numerous shales in the Mining Research Laboratory, it would appear that the error introduced is negligible in most cases. It is obvious, however, that the correction will give rise to large errors if the sample contains large amounts of undecomposable silicates with an alumina-content differing greatly from that of orthoclase; for this reason alone the method cannot be applied indiscriminately to all rocks. This correction is by no means the only source of error, but before attempting to estimate the magnitude of the errors, comparative tests were made to decide which variation of the rational analysis should be adopted, the two methods chosen being a modification of that of Lunge and Millberg[1] and that of Selvig,[4] with one or two minor alterations.

The modified method of Lunge and Millberg is as follows:—

Mix about one grm. of the finely-powdered material in a platinum dish with 40 ml. of distilled water and 10 ml. of concentrated sulphuric acid. Cover the dish with a clock glass and heat until fumes are given off. Allow fuming to continue for 15 minutes, set aside to cool, dilute with water and allow the mixture to settle. Decant the clear liquid through a filter, retaining as much as possible of the insoluble matter in the dish. To the residue add 1 ml. of concentrated hydrochloric acid and a little water, boil, allow the mixture to settle, decant through the filter and wash. A further extraction with hydrochloric acid may be necessary if much iron is present. Next add 15 ml. of a 10 per cent. solution of sodium carbonate crystals, boil, dilute and decant. Repeat the extraction with another 15 ml. of sodium carbonate solution, then transfer the residue to the filter, wash with water and dilute hydrochloric acid, and, finally, with water. Transfer the residue to a platinum crucible, ignite and weigh. The residue is quartz and undecomposed silicates. The proportion of the latter may be approximately obtained from the amount of alumina present, on the assumption that the undecomposed silicate is orthoclase. The alumina is determined by treating the residue with sulphuric and hydrofluoric acids, evaporating until fumes of sulphuric acid are freely evolved, extracting with water and precipitating the alumina in the usual manner. The weight of alumina, multiplied by 5·41, gives a figure for the felspar which, when deducted from the previous weight of quartz, felspar, etc., gives the proportion of quartz.

The method finally adopted in the Mining Research Laboratory, Birmingham, was that of W. A. Selvig, with one or two minor modifications, the details being as follows:—Five grms. of the sample, ground to pass 60-mesh I.M.M., are mixed with 300 ml. of dilute hydrochloric acid (2·5 per cent. by vol.), and heated to boiling in a deep porcelain dish of 1300 ml. capacity. The dish is allowed to stand for 2 hours, or until the material has settled, and the clear liquid is syphoned off. It is advisable to have a tap or pinch-cock in the syphon tube to reduce the rate of flow towards the end of the operation; if the syphon is clamped so that the end of the short limb is adjustable in the liquid, it will be found possible to remove practically the whole of the solution without disturbing the solid material. The residue is stirred with 100 ml. of water, 100 ml. of sulphuric acid (1 : 1 by vol.) are added, and the mixture is boiled, with frequent stirring, until acid fumes are freely evolved. The temperature of the solution should not rise above 200° C., and the total time of evaporation should be approximately 45 to 60 minutes. The dish is allowed to cool for 30 minutes, and its contents are diluted with a litre of water, well stirred and allowed to settle. The clear solution is syphoned off, and the residue is treated with 100 ml. of water and 100 ml. of the sulphuric acid and evaporated once more. After dilution, and settling and syphoning off the solution, the residue is neutralised with Lunge solution. If the amount of acid liquid remaining in the dish is large (20 ml. or more), 50 per cent. sodium hydroxide solution should be used for neutralisation, to prevent excessive dilution of the Lunge solution in the following operation. Three hundred ml. of Lunge solution are then added, and the liquid is heated to boiling, with frequent stirring. After standing for two hours the solution is syphoned off, and the residue is boiled for 5 minutes with 500 ml. of concentrated hydrochloric acid, diluted to one litre, and allowed to settle. The acid solution is syphoned off, the residue is neutralised with Lunge solution or 50 per cent. sodium hydroxide solution, 150 ml. of Lunge solution are added, and the liquid is heated to boiling. After standing for two hours, the Lunge solution is syphoned off, and the residue is boiled for five minutes with 200 ml. of concentrated hydrochloric acid. Two hundred ml. of water are then added, and the liquid is filtered through a Whatman No. 40 filter. The residue is transferred to the filter, washed twice with hydrochloric acid (1 : 3 by vol.) and then with water, until the washings are free from chlorides, and, finally, ignited to constant weight in a tared platinum crucible. To the ignited residue are added 5 ml. of water, 5 to 10 drops of concentrated sulphuric acid and 15 ml. of hydrofluoric acid, and the resultant liquid is evaporated on a hot plate until sulphuric acid fumes are evolved. The evaporation is repeated with two further quantities of hydrofluoric acid, heating being continued during the final evaporation until sulphuric acid fumes are *freely* evolved, to ensure complete removal of fluorine, which would interfere with the determination of alumina in the residue. The contents of the crucible are extracted with water, and the solution is filtered. The alumina in the extract is then determined in the usual way by precipitation with ammonia, methyl red being used as indicator to avoid excess.[5] The weight of alumina, multiplied by 5·41, gives the equivalent weight of potash felspar, and this, subtracted from the weight of the ignited residue previously determined, gives the amount of quartz or free silica in the sample.

The above method differs from that of Selvig in the use of a syphon in preference to decantation, the grinding of the sample to pass 60-mesh I.M.M. instead of 200, and the removal of silica from the residue by evaporation with hydrofluoric acid instead of by fusion with sodium carbonate and separation of the silica by evaporation to dryness with hydrochloric acid.

Four samples were analysed by each method, the results being shown in Table I. Although the results obtained with two samples agreed well, those obtained with samples R.121 and R.122 differed greatly. Duplicate analyses by Selvig's method gave consistent results, whereas those obtained by the Lunge method showed great variations. As a further check, Dr. Francis supplied results of analyses of two of the samples carried out in the Government Laboratory by Lunge's method and by Selvig's method. The results, also given in Table I, bear out the fact that Selvig's method is capable of giving consistent results, whilst that of Lunge is not.

TABLE I

COMPARISON OF THE MODIFIED LUNGE AND SELVIG METHODS FOR FREE SILICA

	Free SiO_2	
Sample	Lunge method Per Cent.	Selvig method Per Cent.
R.121	52·6	26·1
	50·6	25·8
	48·0	28·2*
	38·2*	25·2*
R.122	36·9	21·3
	46·2	20·1
	43·3	21·9*
	44·8*	19·3*
R.123	4·0	4·5
	29·8*	4·5
"Greys"	71·0	71·4
	68·7	71·1

* Figures supplied by the Government Chemist.

As it was apparent that Lunge's method was liable to give rise to large errors, a test analysis of pure china clay was made by this method, silica and alumina being determined in the various acid and alkali extracts. Table II shows the amount of silica and alumina in the different extracts, compared with the ultimate analysis of the kaolin. It will be seen that, whilst all the alumina had been extracted (which would indicate complete decomposition of the kaolin), only half the silica had been removed, the remainder passing on to the residue, and so giving rise to a high figure for the quartz present. The actual result obtained was roughly 20 per cent. of free silica by this method, whilst that of Selvig gave a result approximately nil. It was evident from this that the alkali treatment in Lunge's method was insufficient to remove the silica that resulted from the decomposition of the kaolin, and that the high results obtained in the case of samples R. 121 and R. 122 were probably due to this cause. As a result of these tests, it was decided to adopt Selvig's method, and investigations were begun with a view to estimating the magnitude of the errors which might arise.

TABLE II

SILICA- AND ALUMINA-CONTENTS OF ACID AND ALKALI SOLUTIONS OBTAINED DURING RATIONAL ANALYSIS OF KAOLIN BY THE LUNGE METHOD

	Silica Grm.	Alumina Grm.
Sulphuric acid extract ..	0·0030	0·1798
Hydrochloric acid extract ..	0·0031	0·1892
Lunge solution extract ..	0·2334	0·0034
Total extracted	0·2395	0·3724
Ultimate analysis of kaolin ..	0·4833	0·3678

From a consideration of the analytical procedure given above it will be seen that the chief sources of error are:—(i) Mechanical loss of quartz through syphoning; (ii) loss of quartz by solution in alkali; (iii) incomplete decomposition of minerals present other than quartz; (iv) incomplete removal of the products of decomposition.

Rational analyses of samples of quartz showed that mechanical loss and loss due to solution in alkali amounted to 1·2 per cent. with quartz ground to 60-mesh I.M.M., and to roughly 6 per cent. with quartz ground to 200-mesh. The effect of the solvent action of the alkali alone was determined by treating quartz and several shale samples with Lunge solution as in the rational analysis procedure, the extract being filtered and the dissolved silica determined by evaporation with sulphuric acid in the usual way. Table III shows that the maximum amount of silica extracted from the shales is 1 per cent., and that with quartz through 200-mesh, only 2 per cent. is dissolved from a 5-grm. sample. As only 6 per cent. is dissolved from 0·5 grm. of quartz it would appear that only the finer quartz particles go into solution, and that when shales are ground to pass 60-mesh I.M.M. the amount of fine quartz produced is insufficient to cause any large error due to solution in alkali. The error may have been appreciable when the method was used for the rational analysis of clays, the average diameter of the particles of which is less than 0·002 mm., but with coal-measure rocks and shales the grain size is greater than 0·001 mm., and, as a result, the solubility of the quartz particles in Lunge solution is inappreciable. Moreover, if desired, a correction for this error may be applied by making a solubility test of the sample in Lunge solution.

The third source of error, *viz.* incomplete decomposition of minerals other than quartz, is always present, for the residue obtained from the rational analysis never consists entirely of quartz. A number of minerals were, therefore, subjected to the rational analysis treatment in order to obtain information regarding the amount of decomposition that takes place under such conditions. As it was manifestly impossible to check the action of the rational analysis treatment on all known minerals, only those minerals that are likely to occur in shales in any great amount were tested. Table IV shows the amount of decomposition that takes place when various minerals are subjected to the method of rational analysis, together with a partial analysis of the minerals before and after decomposition.

TABLE III

EFFECT OF LUNGE SOLUTION ON QUARTZ AND VARIOUS SHALES

		Free silica Per Cent.	Silica dissolved Per Cent.
Quartz (5 grms., 200-mesh)		100	2·07
Quartz (0·5 grm. 200-mesh)		100	6·2
Llay Main "Hard rock,"	60-mesh	44·6	0·64
,, ,, White shale	,,	20·2	0·69
,, ,, Grey shale	,,	27·5	1·03
,, ,, Floor	,,	22·1	1·04
,, ,, "Hard rock"	,,	38·9	0·77
New rock gritstone	,,	69·7	0·67
Cannock Chase shale	,,	30·8	0·72
Pennant rock	,,	52·9	0·48
Cannock Chase siltstone	,,	49·4	0·43
Cannock Chase siltstone	,,	59·4	0·42

It will be seen that olivine, epidote, nepheline, muscovite, biotite, haematite, limonite, magnetite and ilmenite are practically completely decomposed by the treatment, whilst hornblende, augite, tourmaline and garnet are only partly decomposed, the quartz and felspar group being almost unaffected. The minerals which may possibly occur, therefore, in the residues from rational analyses of shales are quartz, the felspars, hornblende, augite, tourmaline, garnet, rutile, and barytes. Actually, in the course of the analysis of numerous samples of shales and coal-measure rocks from widely different areas, experience has shown that the residues contain little or no iron, which would indicate that hornblende, augite, tourmaline, and garnet do not occur to any appreciable extent in the residues. Assuming, however, that they do, consideration of the alumina-contents will show the maximum error likely to be introduced by the assumption that the residue consists of quartz and felspar only. Analyses of shales have shown that the residues rarely contain 0·1 grm. of alumina, ferric oxide, etc., and, assuming that this amount is the maximum likely to be encountered, the correction to the residue for "felspar" present would be approximately 11 per cent. If, however, in an extreme case the alumina, iron, etc., had actually been derived from tourmaline or anorthite (Al_2O_3, Fe_2O_3, approx. 40 per cent.), then, to obtain correct figures for the quartz present, the appropriate factor 2·5 must be employed, and the correction would then be roughly 5 per cent. Thus the error introduced by the assumption, that the residue consists of quartz and orthoclase, would in this case be approximately 6 per cent. In practice, the normal correction that has to be applied is of the order of 3 per cent., so that, even in the extreme case above, the possible error introduced by the correction is less than 2 per cent. In most cases it is undoubtedly much less, as is shown by the absence of iron from the residues. The above remarks apply only to analyses of coal-measure rocks and shales. When the rational analysis is applied to igneous rocks the correction is responsible for errors sometimes amounting to 20 per cent., so that absurd results are obtained.

TABLE IV

EFFECT OF "RATIONAL ANALYSIS" ON QUARTZ, FELSPAR, ETC.

	Decomposition		Analysis of mineral		Analysis of residue	
Mineral	Through 60-mesh on 100-mesh Per Cent.	Through 200-mesh Per Cent.	SiO_2 Per Cent.	Al_2O_3 Fe_2O_3 Per Cent.	SiO_2 Per Cent.	Al_2O_3 Fe_2O_3 Per Cent.
Quartz	1·2	5·8	97·31	0·90	98·53	0·78
Flint	3·2	7·2	—	—	—	—
Chalcedony	3·3	7·3	—	—	—	—
Opal	58·3	59·4	—	—	—	—
Orthoclase	3·4	7·7	64·04	20·83	65·51	19·79
Albite	1·0	5·1	66·90	21·58	67·27	21·12
Oligoclase	3·4	8·2	—	24·88	64·69	23·33
Olivine	98·2	94·3	40·21	11·18	58·83	14·47
Hornblende	21·3	35·0	46·64	25·70	51·47	23·25
Epidote	44·7	90·4	39·32	34·95	67·13	20·87
Nepheline	97·4	95·9	40·36	35·96	51·23	21·16
Muscovite	79·8	93·0	43·67	39·95	64·46	27·17
Biotite	—	98·1	38·54	44·75	71·43	20·53
Augite	—	57·4	41·66	22·43	50·03	11·60
Tourmaline	3·9	15·5	36·23	41·41	36·59	41·28
Kaolin	—	90·7	48·33	36·78	72·02	19·07
Haematite	99·9	99·9	—	—	—	—
Limonite	99·8	99·6	—	—	—	—
Magnetite	99·7	99·7	—	—	—	—
Ilmenite	99·8	99·6	—	—	—	—
Rutile	4·4	27·8	—	—	—	—
Barytes	3·4	29·4	—	—	—	—
Garnet	42·4	86·4	—	—	—	—
Sericite	64·4	63·8	59·24	26·56	94·51	3·58

The fourth source of error, *viz.* incomplete removal of the products of decomposition, tends to give high results. This has been found to be due almost entirely to the incomplete removal of the silica resulting from the decomposition of silicates present in the sample under analysis, and confirmation of this is afforded by the results given in Table IV. It will be observed that the silica-content of the treated mineral is invariably greater than that of the original material, the increase being greatest in cases where the mineral has been most affected by the treatment. The greatest increase is equivalent to 0·1 grm. of silica, which would, in the course of the ordinary analysis, produce a positive error of 2 per cent. It has since been found, however, that, by practically complete removal of the acid extracts during analysis, neutralisation with 50 per cent. sodium hydroxide solution, and washing the residues, if necessary, by decantation before neutralisation, the concentration of the Lunge solution can be kept constant, thus avoiding the dilution which neutralisation of excessive quantities of acid extract entails, with the consequent incomplete solution of the hydrated silica.

From the above experiments it would appear that the rational analysis for free silica, when applied to coal-measure rocks and shales, tends to give low results. With samples ground to 60-mesh I.M.M., mechanical loss and solution of quartz in alkali solution may reach a maximum of 1 per cent., and the correction applied to the residue may introduce an error of approximately 1¼ per cent. in most cases, whilst incomplete removal of hydrated silica should not, with careful work, be responsible for errors larger than 1 per cent. As the first two errors are counteracted by the last, the probabilities are that the method can in general be relied upon to give results accurate within 2 per cent.

As a further test, Dr. Francis, of the Government Laboratory, and Mr. Clarence A. Seyler kindly collaborated in the analysis of samples by the rational analysis method. The results, which are given in Table V, show that agreement to 1 per cent. may be obtained by different analysts.

TABLE V

COMPARISON OF RESULTS OBTAINED FOR FREE SILICA BY DIFFERENT ANALYSTS

	Analysts			
Sample	No. 1 Per Cent.	No. 2 Per Cent.	No. 3 Per Cent.	No. 4 Per Cent.
1	—	Nil	0·5	—
2	5·9	8·0	7·5	—
3	19·1	19·4	20·4	—
4	28·7	—	30·8	—
5	48·8	42·5	43·1	—
6	28·2	25·2	26·0	—
7	21·9	19·3	20·7	—
8	61·0	58·8	59·0	—
9	72·5	70·4	71·2	—
10	Nil	Nil	Nil	—
11	38·6	38·2	37·7	37·7
12	36·4	35·6	38·0	38·0

ULTIMATE ANALYSIS.—Attempts have been, and, apparently, are being made at the present time, to calculate the free silica-content of a shale from its ultimate analysis. Although this analysis can be made with a high degree of accuracy, it is fallacious to assume that calculations based on the analysis must necessarily give accurate results. The widely divergent results that may be obtained by this method are shown in Table VI, where the free silica-content of several samples has been calculated, the minerals present being assumed to be, in the one case, quartz, felspars, kaolin, etc., and, in the other, quartz, micas and kaolin. Unless the chemist is supplied by the mineralogist with a list of minerals present in the rock, he has no definite facts on which to base his calculations, and with shales it is apparently extremely difficult to identify all the minerals present, even by microscopical examination.

TABLE VI

FREE SILICA-CONTENT OF COAL MEASURE ROCKS BY CALCULATION FROM ULTIMATE ANALYSIS

Sample	S.33 Per Cent.	S.32 Per Cent.	"Greys" Per Cent.	S.54 Per Cent.	
Silica	54·32	59·88	81·98	23·99	
Alumina	24·35	21·98	6·77	12·32	
Ferric oxide	4·27	4·62	6·33	31·18	
Lime	1·26	0·53	0·47	1·04	
Magnesia	0·69	1·60	0·36	2·43	
Potash	4·02	3·92	0·74	0·64	
Soda	0·73	0·66	1·90	0·01	
Loss on ignition	10·28	6·63	2·48	23·71	
Calculated free silica-content	11·4	19	64·2	4·0	Composition assumed to be quartz, felspars, kaolin, &c.
	17·6	34·8	67	11·5	Composition assumed to be quartz, micas, kaolin, &c.

Microscopical examinations of many of the coarse-grained rocks analysed by the rational analysis method have been carried out by Mr. S. H. Shaw, of the Geological Department, Birmingham University, and micrometric measurements have been made of the free silica. The results to hand at the moment show fair agreement with those of the rational analysis. It was hoped that a further check might be obtained by *X*-ray analysis of the samples, but information from the laboratories of Professor W. Bragg, of Manchester, is to the effect that results by this method have not a greater accuracy than ±5 per cent., so that no useful purpose would be achieved by having analyses made in this way.

It seems clear that, of the methods reviewed for the determination of free silica in coal-measure rocks, the method of rational analysis, when properly carried out, is by far the most reliable at the present time. Though the results obtained may be low by amounts up to 2 per cent., the method appears to be far more accurate than calculations from the ultimate analysis, micrometric measurements of shale sections, or *X*-ray analysis.

In conclusion, I wish to thank Mr. H. V. Thompson and Professor Sollas for their helpful suggestions, Dr. A. G. Francis, Mr. Clarence A. Seyler and Mr. S. H. Shaw for their kind co-operation, and Mr. J. Ivon Graham for his invaluable criticism and advice.

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DISCUSSION

The PRESIDENT remarked that the Society was grateful to Mr. Shaw for the interesting paper on this question. He could realise the importance of the paper, especially if it had any bearing on the question of silicosis.

Dr. W. R. JONES thanked the President for the opportunity of contributing to the discussion of this interesting paper, which contained, in addition to the author's main conclusions, valuable data which had not been previously published. Table IV, for example, brought out very clearly the great variation, under identical chemical treatment, in the relative amounts of solubility of different species of minerals composed entirely of free silica, and also of different silicate minerals. He hoped that a study of that Table would prevent a repetition of such generalisation as made recently elsewhere, that free-silica minerals were more easily soluble in the lung than natural silicates. There were several minerals composed of free silica with widely varying degrees of solubility; there were dozens of natural silicates, also with very marked differences of solubility. The speaker did not think it was helpful, in the study of silicosis, to base far-reaching conclusions as to what happened in the lung, on such a sweeping generalisation, which had long been refuted by mineralogists.

He could not agree with the author's conclusion that the determination of the free-silicate content of coal-measure rocks by the method of rational analysis advocated in the paper, or by any other method of rational analysis, was more reliable than that obtained by complete chemical analysis followed by the allocation of the constituents to the actual minerals present in the rock. On the contrary, he believed, with other geologists, the reverse to be the case, and for this reason: the rational analysis was based on the erroneous assumption, as had been pointed out many years ago by geologists, that the alumina in many of these rocks could be allocated to potash felspar. Many coal-measure rocks, particularly those in the working-places in the anthracite collieries of South Wales (where 90 per cent. of all cases of silicosis in the British coal-mining industry occurred) contained no potash felspar at all; that mineral had been completely converted into sericite. Now the ratio of alumina to silica in sericite was as 1 is to 1·243, whereas in potash felspar this ratio was as 1 to 3·5; in other words, almost three times as much silica would be allocated to the alumina on the purely hypothetical and incorrect assumption that it was present as potash felspar, as would be the case when the silica was allocated to the alumina in the ratio for the mineral known to be abundantly present in these South Wales rocks.

Dr. Jones here showed on the screen a photomicrograph of a typical sandy shale from a colliery that was notable for the number of cases of silicosis contracted there. This sandy shale contained no potash felspar, but hundreds of fibres of sericite were clearly visible. He would ask how was it possible, with such a rock, to obtain the percentage of free silica by allocating the alumina, according to the rational analysis method, to potash felspar? He could understand the attraction of a method which would enable analysts to return the consistent results referred to in the paper, but would point out that the consistency was obtained by arbitrarily multiplying the alumina-content, in all these cases, by 5·41. With this type of rock the results would be consistently low in the free-silica content. Moreover, these rocks often contained one per cent. or over of titanium oxide, weighed as alumina by the rational analysis method, and this further contributed to lowering the percentage of free silica.

The unreliability of this arbitrary allocation of alumina could be seen in Table VI, where a difference of 17·2 per cent. (34·8 minus 17·6) was shown between the free-silica content of the first two samples. Yet the difference given in the potash content was only 0·1 (4·02 minus 3·92). Similarly, in the same Table, under S. 33, two arbitrary allocations of the same analysis showed a difference of 15·8 per cent. (34·8 minus 19) of free silica. He would ask the author if the figure 34·8 was not a misprint for 24·8, or thereabouts? He would like to put it on record that geologists in all countries, who had studied this question, had no faith in the results of rational analysis of certain types of rocks, such as many of the coal-measure rocks, and had frequently said so.

The speaker's criticism of parts of the paper did not, however, prevent him from congratulating the author on a valuable piece of research. The author had definitely shown that Lunge's method was unreliable, and had established that, by his modification of Selvig's method, it was possible, with rocks of certain types, to obtain the *relative* (not, the speaker submitted, the *actual*) percentages of free silica: that was a distinct advance on any other rational analysis method and would probably prove of economic importance in the pottery industry.

Dr. HALDANE remarked that Dr. Jones had referred to a statement of his (Dr. Haldane's) at a discussion of the Institution of Mining and Metallurgy, about the solubility of silica and other minerals. He thought Dr. Jones's statement was extremely misleading, but perhaps Mr. Shaw would deal with that later. In the Selvig method the stone being analysed was treated with strong acid again and again in order to decompose the silicates, so far as possible, but was not treated with strong alkali for two hours. The alkali was mainly sodium carbonate, and was used in weak solution in order to minimise the solution of pre-existing free silica present in the stone. Great precautions were taken not to dissolve any more of the free silica pre-existing in the rock than could be helped, and the figures given showed the amounts which were, nevertheless, dissolved in the not strongly alkaline solution. He was not going into the very vexed question of silicosis that evening, because it was a medical question, and he would not refer to it except to say that he disagreed very thoroughly and completely with Dr. Jones's conclusion on that point (not expressed at this meeting, but in another paper).

Dr. R. LESSING said that he thought that the difficulty about the so-called "rational" analysis was that the substances which one liked to isolate were destroyed in the course of this procedure, and that, he thought, was the main criticism which Dr. Jones had to make on the work put before the meeting. As one destroyed practically all the silicates, the only original material left over was free silica. Now, a true "rational" analysis would be something on the lines of the Sollas method. Apparently this method was not very accurate, and did not give good results. At the same time he would like the author to consider whether, by certain refinements which might be applied, the specific gravity separation in different solutions might be brought to such a pitch of perfection that the ideal of obtaining the original constituents of the sample in isolated form might be reached or approached. Then Dr. Jones and his brother geologists might be satisfied. On the other hand, he thought that it was quite clear that ultimate analysis to which certain arbitrary calculation was applied could not give them the results they would like to have.

From the point of view of silicosis, although that was not to be considered that evening, it might be interesting to know whether the method had been applied to silicotic lungs. One point in connection with Table IV had struck him rather forcibly, and it might, perhaps, furnish a bridge over the chasm between Prof. Haldane and Dr. Jones, on the question whether silicosis was caused by free silica or by other minerals such as sericite. Of all the materials examined in Table IV, it happened that sericite was the only one which left a residue containing 94 per cent., or something approaching the silica-content of pure quartz. That might be significant or not for its physiological effect. On the other hand, Dr. Jones had taken it for granted that only a small percentage of sericite was left as residue. He personally made it 35 to 37 per cent. Perhaps this might be worth very serious examination. It might be found that sericite, after all, would furnish a residue even without this drastic chemical treatment, which left the silica behind not differing greatly in composition from quartz. The investigation might be carried further in this direction. He differed from Dr. Jones, whose work he admired, in his criticism of the methods applied in this course of analysis. He appreciated his argument on the shortcomings of rational analysis from the point of view of the mineralogist. He thought, however, that the behaviour of the petrological entities under the chemical treatment applied to them might, on further study, give some indication of what was likely to happen, say, to quartz and sericite, when subjected to biochemical reactions in the lung tissue or the lymphatic juices.

Mr. E. M. HAWKINS, speaking from the purely chemical side, said it had been his fortune (or misfortune) to have to do such analyses lately, and the Selvig method, as originally put forward, was a very long business, particularly where one had to work single-handed. He, therefore, thanked the author for speeding up the process. It should be remembered that, as a rule, the alumina found was from 0·3 to 0·9 per cent., so that with the factor 5·41 the amounts of felspar would be between 2 and 5 per cent. If this alumina should really be calculated to some other mineral than potash felspar and another factor should be used, the error in the "free silica" would not amount to more than 2 or 3 per cent. at the outside. He did not think that Dr. Jones's criticism was quite justifiable, for the purpose of these analyses was to show the difference between one shale and another. He thanked the author for this very interesting paper, and particularly for the way in which he had traced the various errors likely to occur, so that by the final method comparable results could be obtained.

Professor BOSWELL welcomed the account of methods of rational analysis described by Mr. Shaw, and expressed the hope that chemists would be able to develop them further, so as, if possible, to avoid the methods of calculation that had been criticised that evening. The amount of error introduced into the estimation of constituents other than free silica by multiplying by a theoretical factor depended, of course, on the quantity of silica in the rock. If the rock happened to be a high-silica material, the error would be small. The geologists' method of determining the mineral composition was to interpret the rational analysis by separation and examination under the microscope of the constituents. They recognised, however, that this was not an entirely satisfactory method, for while minerals could be separated from coarse-grained rocks, the technique became more and more difficult with fine-grained rocks, such as clays and shales. Although work was proceeding in this field, no technique was at present satisfactory. On the other hand, calculation of composition from chemical analysis was not a safe procedure. He (the speaker) therefore appealed for the extension of the methods of rational analysis, so as to avoid, if possible, the use of factors such as 5·41 for orthoclase felspar. In this connection he had had, during the war, to investigate the resources of potash in this country. Theoretically pure potash felspar should show 16·9 per cent. of potash, but if apparently pure samples yielded more than 10 per cent. of potash, they were exceptional. Thus the composition of even an individual mineral varied considerably from the theoretical figure given in the text-books.

Dr. B. S. EVANS asked if the fuming with sulphuric acid in Mr. Shaw's process was essential; obviously it would tend to dehydrate the silica, thereby rendering it more difficult to dissolve in the alkaline solution afterwards employed.

Mr. J. I. GRAHAM said that he would like to say a few words regarding the amount of time Mr. Shaw had put into this work. The subject seemed, perhaps, to be treated scantily in the paper, but he knew what a long time had been spent on the investigations and how carefully Mr. Shaw had gone into the various points. Another direction in which the rational-analysis method had been applied in the

Mining Research Laboratory was for the examination of the very small samples of dust which they were collecting from the air in mines. The analysis was done on 0·15 grm. instead of on 5 grms., as advised by Mr. Shaw, and the same procedure was followed, with the exception that they centrifuged before decanting. When they got down to the final residue, which they assumed was felspar plus free silica, they had recourse also to treatment with hydrofluoric acid. The total residue should have been alumina plus potassium sulphate, and a factor based on that assumption was used, *viz.* 2·01. The results agreed very well indeed with treatment as carried out by the method described by Mr. Shaw, in which the test was made on 5 grms. This work was done by Dr. Skinner, and he (Mr. Graham) felt that it supported the claim that the rational-analysis method, as advised by Mr. Shaw, was reasonably accurate. The quantity of felspar was only comparatively small and the error was not great. The error in any other known method for determining free silica was so great that it was worth while having a method like that of rational analysis, even if it were only correct within about 2 per cent.

Mr. SHAW, replying, said that Dr. Jones had referred to the action of alkalis on quartz and silicate minerals. It was a definite fact that quartz and other forms of free silica were more soluble than silicate minerals in alkaline solutions.

The work of Lunge, Schwartz and Doelter had shown that, whilst quartz was appreciably soluble in boiling sodium carbonate solution, it was necessary to digest the felspars with sodium carbonate solution under pressure at 200° C. for some weeks before they were attacked. Table IV showed the effect of acid treatment on various minerals. The extraction with Lunge solution was necessary to dissolve the hydrated silica resulting from the decomposition of the silicates by acids and had little or no effect on the silicates.

Referring to the question of calculations from the ultimate analysis, he wished to point out that the felspars had not been calculated from the alumina. He had followed the geological method of calculating the Norm, and had calculated the amounts of felspars, in the one case, and micas, in the second case, from the potash, soda and lime contents of the sample. Excess alumina had been assigned to kaolin and the remaining silica calculated as quartz.

He did not agree that it was erroneous to assume that the alumina in the residue from a rational analysis came from felspar. He had examined a number of samples from the anthracite district in South Wales, and the residues contained less than 1 per cent. of felspar. If, as Dr. Jones stated, these rocks contained sericite, then these analyses confirmed the fact that sericite was decomposed by the rational-analysis treatment, as he (the speaker) had thought from the results shown in Table IV. The high silica-content of the residue after treatment of the sericite by the rational analysis method was due, in his opinion, to the fact that the sample was not pure. It was extremely difficult to obtain pure specimens of many minerals, and if anyone could supply him with a sample of pure sericite he would be extremely grateful.

He disagreed with Dr. Jones's remarks concerning titanium oxide. Whilst titanium oxide was a common constituent of rocks, it was not present in amounts greater than 1 per cent. in the majority of cases. Moreover, ilmenite was completely decomposed by the rational-analysis treatment and rutile was partly decomposed, so that it was by no means obvious that the "1 per cent. or more of titanium oxide" would remain in the residue and be subsequently weighed as alumina.

The rational analysis, so far as he personally was concerned, was merely a means of determining the free-silica content of rocks and shales, and he was not interested in the amount of felspars or micas present, except in so far as it enabled him to apply a correction to the residue and so obtain a more accurate result for the free silica. He had used a modification of the rational analysis, introduced by

Mr. Graham and Dr. D. G. Skinner for the analysis of small samples, to estimate the free silica in the residue from a silicotic lung. Although duplicate analyses agreed well, he was not inclined to put too great faith in the method, as he thought that the result was considerably below what it should be, owing to solution of the fine quartz particles in the Lunge solution. Professor Sollas's method had been applied to English rocks with considerable success, but it did necessitate the presence of coarse-grained rocks. He had tried to improve the separation of fine-grained rocks by using a centrifuge, but had not met with much success. In any case, attempts to separate quartz from coal-measure rocks by this method were not likely to be successful, as there was always the possibility of the presence of soda-lime felspars in the rocks with specific gravities approximating closely to that of quartz.

He agreed with Professor Boswell's remarks concerning the calculation of the composition of a rock from the ultimate analysis. As a help to geological classification the method was, perhaps, useful, but his problem was to determine the actual amount of quartz present, and the geological Norm might have no relation at all to the actual mineral constituents of a rock.

With regard to the point raised by Dr. Evans, he agreed that excessive treatment with sulphuric acid might result in dehydration of the silica, with subsequent incomplete solution in Lunge solution. That was the object of controlling the temperature of the acid at 200° C. The idea of the method was to decompose all silicate minerals, necessitating strong attack with acid, and to remove the products of decomposition. He was of the opinion that fuming with sulphuric acid below 200° C. did not affect the solubility of the hydrated silica in alkali solution. The analyses of the residues of minerals (through 200-mesh) after treatment, given in Table IV, showed that a certain amount of silica remained undissolved, but the greatest amount was only equivalent to 0·1 grm. or 2 per cent. on the original sample.

Mr. Clarence Seyler wrote as follows:—The paper of Mr. A. Shaw is of great interest and importance, in view of the problem of the relation of silicosis to the amount of "free silica" in rocks. It confirms my opinion that the method of "rational analysis," as applied to argillaceous rocks, is the best available, if properly carried out with the precautions mentioned by Mr. Shaw. One of the most important points is the careful regulation of the temperature during the digestion with sulphuric acid. A thermometer should always be immersed in the liquid and the process carefully watched, so that the temperature does not exceed 200° C. Since adopting this precaution I have had no difficulty in getting reasonably consistent results. The objection that finely-divided quartz may pass into solution in the treatment with the alkaline solution is met by extracting the original material under the same conditions with the alkali and determining the dissolved silica. In my experience the amount so dissolved is small.

The only assumption involved in the method is that the "felspathic residue" has the composition of orthoclase, and can be calculated from the alumina. Since, however, the amount of alumina in the residue is nearly always small, the possible error from the assumption is also small. It can be minimised by making a complete analysis of the residue. No careful analyst would omit a petrographical examination of the specimen. In my experience the estimate of the quartz formed by experienced petrologists agrees remarkably well with the "rational analysis." It is a far simpler proposition to estimate the percentage of quartz from the ultimate analysis of the residue than from that of the original rock. The ferromagnesian minerals have been mostly removed, as well as the decomposable minerals which form the "argillaceous matter"; these are difficult to identify under the microscope and very variable in composition.

The determination of the amount of "free silica" (by which quartz is, no doubt, meant) has apparently lost some of its importance since the Silicosis Order has altered the definition of a "silica rock," which was formerly defined as one containing over 50 per cent. of quartz. In reality, however, I do not see how a "silica rock" can be defined without reference to the amount of quartz it contains. The classification of sedimentary rocks by geologists is in a very unsatisfactory condition. This had no great practical importance until the question of silicosis arose. I do not wish to offer an opinion upon what silicosis is and whether it is due to "free silica" or to silicates. As matters stand, however, it is very important to have working definitions of "silica rock," sandstone, grit (or "gritstone"), shale, and rocks of intermediate character. I do not think that such definitions should present insuperable difficulties. Sand and grit can be reasonably defined by the range of size of the particles. For most purposes only quartzose sand need be considered. To define a sandstone, not only the percentage of quartz and the size-range of the particles, but also the compactness of the rock would have to be considered. Loose sand is to the geologist a "rock," but it is not a stone. Probably the hardness could be used for purposes of differentiation, if a satisfactory measure of it were adopted. Rittinger's law, connecting the hardness with the work done in crushing, grinding or breaking and the new surface produced, would probably be useful, since the surface depends upon the fineness of the particles, especially those of the smallest size, which are the most dangerous. In any case, it appears to me that a siliceous sandstone must consist chiefly of quartzose particles, that is, as a dividing line must contain over 50 per cent. Thus the work of Mr. Shaw supplies us with a fair measure of at least one of the factors in the definition.

Mr. N. SIMPKIN sent the following contribution to the discussion:—
I have read the paper by Mr. A. Shaw with considerable interest, particularly in view of the fact that Mr. Graham of the Mining Research Laboratory at Birmingham was good enough some time ago to forward me full details of the method which Mr. Shaw has been using for the determination of free silica.

We have carried out a number of determinations of the free-silica content of various types of coal-measure strata from the Lancashire coalfield by the method which Mr. Shaw is using, and have found that in duplicate determinations very satisfactory agreement can be obtained; for example, with a rather highly siliceous shale duplicate tests yielded 43·26 and 43·89 per cent. of free silica, whilst another shale yielded 24·96 and 25·15 per cent. of free silica.

A further test of the method was made by comparing the results thus obtained with the results of the microscopical examination of certain coal-measure rocks. The latter determinations were made independently in the Palaeobotanical Laboratories of the Lancashire and Cheshire Coal Research Association, and the following table gives the results obtained with Mr. Shaw's method, as compared with micrometric measurements of the free silica. The latter method fails, however, when the grains of the rocks are of a certain fineness. With coarse and medium-grained rocks, however, it will be seen that very good results were obtained.

Material	Free Silica Chemical Method	 Microscopical Method
1. Siliceous shale	43·6	46·0
2. Mud stone	20·5	Grain-size too fine
3. Fine-grained shale	22·3	
4. Argillaceous sandstone	49·6	52
5. Sandstone	75·8	75·0

The agreement in the above table is good, particularly when it is realised that the determination by the chemical method was made on a piece of the material about half-an-inch thick cut out of a lump of the rock, the microscopical method being employed on the adjoining face from which this piece of rock was cut.

The Determination of Small Quantities of Germanium in the Presence of Arsenic

PART I

By S. A. COASE, B.Sc.

(*Read at the Meeting, May* 2, 1934)

It is known (Müller and Smith, *J. Amer. Chem. Soc.*, 1922, **44**, 1909) that germanium dioxide is reduced to monogermane, GeH_4, more readily in alkaline than in acid solution, but the electrolytic reduction in alkaline solution has not been attempted. Since arsenates are not ordinarily reduced in alkaline solution, the following investigation was carried out in order to develop a method for the rapid detection and determination of small quantities of germanium in the presence of large quantities of arsenic.

Germanium occurs widely, but in insignificant amounts (Petar, *Bureau Mines, Information Cir.*, 6401, for general information and list of minerals). Leaving out of account spectrographic methods, 0·1 mgrm. of the metal can be detected by precipitation as sulphide with hydrogen sulphide (Browning and Scott, *Chem. News*, 1917, **116**, 250), or by reducing a germanic salt to germanous oxide, using zinc and sulphuric acid (Bardet and Tchakirian, *Compt. rend.*, 1928, **186**, 637). Quantities of the order of 0·06 mgrm. of germanium have thus been detected in the Marsh type of apparatus (Müller and Smith, *vide supra*). Using sodium amalgam as the source of nascent hydrogen, they reduced germanium dioxide to monogermane, and, by thermal decomposition of the gas, obtained a mirror of metallic germanium in a combustion tube; this operation occupied 60 minutes. The detection in the presence of arsenic was not considered.

For the determination of germanium the following methods are available:

(i) Johnson and Dennis (*J. Amer. Chem. Soc.*, 1925, **47**, 790) precipitate germanium sulphide from 6 *N* sulphuric acid by means of hydrogen sulphide, and oxidise the sulphide with 3 per cent. hydrogen peroxide to the dioxide, in which form it is weighed.

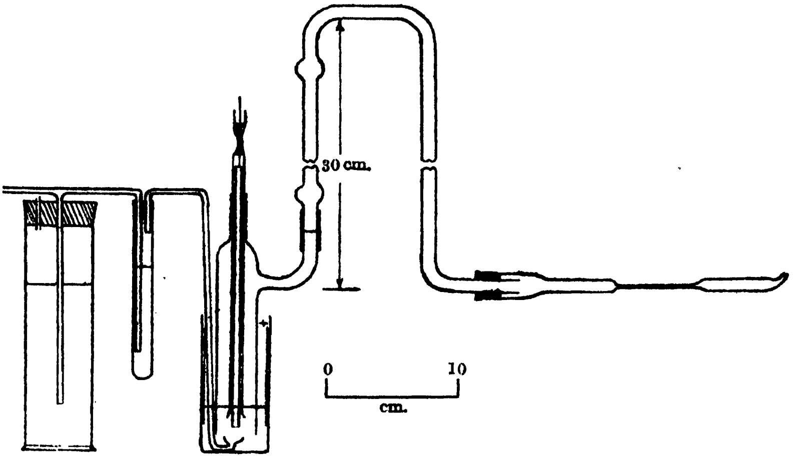
(ii) Müller (*J. Amer. Chem. Soc.*, 1922, **44**, 2493) adds to a solution of the dioxide a small excess of magnesium sulphate, and then ammonium sulphate, followed by ammonium hydroxide. The mixture is boiled for a few moments and allowed to settle for 10 to 12 hours, and the precipitate of magnesium orthogermanate, Mg_2GeO_4, is filtered off, washed, ignited, and weighed in this form.

(iii) Müller and Eisner (*Ind. Eng. Chem., Anal. Ed.*, 1932, **4**, 134) proposed the precipitation of germanium sulphide from 6 *N* sulphuric acid solution by means of hydrogen sulphide, and subsequent hydrolysis by means of boiling water to germanium dioxide. It may be noted here that Abrahams and

Müller (*J. Amer. Chem. Soc.*, 1932, **54**, 86) claim quantitative separation of germanium and arsenic by using weak sulphuric acid (0·09 *N*), and passing hydrogen sulphide through the solution, when arsenic is precipitated (as a sulphide), but not germanium. Then the concentration of the acid is increased to 6 *N*, and the treatment is continued as described above.

(iv) Tchakirian (*Compt. rend.*, 1928, **187**, 229) has proposed two volumetric methods for the determination of germanic acid: *A*. In the presence of alcoholic compounds (mannitol, glucose, glycerol) the solubility of germanium dioxide is increased by the formation of germano-organic compounds. The liquid is titrated with sodium hydroxide solution, phenolphthalein being used as an indicator. *B*. A method based on the liberation, by mannitol-germanic acid, of iodine from a mixture of potassium iodide and potassium iodate. The reaction is complete in 12 hours, and the solution is then titrated with sodium thiosulphate solution.

NEW METHOD.—The method adopted in the present investigation was based on that described by Grant (ANALYST, 1928, **53**, 626) for the determination of antimony as stibine, but it was found necessary to replace the porous pot by a bell, since otherwise cataphoresis of the alkaline solution makes the method impracticable. The apparatus used is shown in the figure.



The cathode consists of a rod of nickel enclosed in a glass tube, flared at the end and provided with a small piece of rubber tubing which furnishes a suitable gas lock. From a tube, placed immediately under the cathode, hydrogen passes out. Monogermane formed is quickly carried away in the hydrogen stream to the combustion tube, where it is decomposed by heat. The hydrogen was obtained from a cylinder of the gas, passing through a safety trap and a bubbler. On test it gave a satisfactory blank. The anode is a sheet of nickel folded round against the side of the beaker. The current was obtained from the 200-volt mains with a suitable resistance. The voltage across the apparatus was 35 volts.

PROCEDURE.—The procedure was as follows:—The solution to be electrolysed was placed in the beaker, the hydrogen stream turned on (two bubbles a second were found convenient, this speed being shown by the bubbler), and when the combustion tube, heated on the side of the constriction nearer the apparatus, had reached a dull red heat, the current was switched on. At the end of an experiment the current was first switched off and the passage of hydrogen allowed to continue until all monogermane formed in the cathode compartment had been swept into the combustion tube. The density of the metallic stain was matched against standards previously prepared.

The following conditions were examined to determine the best conditions of work:

(i) *Metal of the Cathode.*—Cadmium, stainless steel and lead gave no results. Magnesium, iron, copper and a specimen of stainless steel used in dentistry gave slight results, whilst nickel alone gave satisfactory results.

(ii) *Strength of Sodium Hydroxide Solution.*—It was found that the best yields were obtained with a dilute sodium hydroxide solution, but a limit is set by the necessity of maintaining a high conductivity. A solution of about 1·5 per cent. strength was used in the experiments described below.

(iii) *Current Density.*—It was found that a high current density favours a good yield of monogermane, but a limit is set by the need to prevent undue heating. With a higher current density it was found necessary to cool the beaker by a stream of water.

Artificial mingling of the anolyte and catholyte was tried. This was done by forcing the catholyte periodically into the anode chamber, the gas exit tube being closed for this purpose by means of a mercury seal. No appreciable effect on the yield of monogermane was, however, detected. When sodium nitrate or sulphate was added to the electrolyte the yield was unaffected. When sodium chloride was present the expected germanium deposit was obtained, but the anode was attacked and a precipitate formed in the beaker. A similar result was obtained in the presence of sodium nitrite, but this time the yield of monogermane was diminished.

DETECTION OF SMALL QUANTITIES OF GERMANIUM.—In these experiments 0·0273 grm. of germanium dioxide was dissolved in 3 ml. of 10 per cent. sodium hydroxide solution and 5 ml. of water. This was made up to 500 ml., and to aliquot parts 10 ml. of 10 per cent. sodium hydroxide were added, the volume being made up to 70 ml. by the addition of water. This solution was electrolysed in the apparatus described. In the last column are given the times for which electrolysis of the solution and heating of the combustion tube had to be continued in order to obtain a mirror of germanium. Results are given in the table below:

GeO_2 Mgrm.	Cathode area sq. cm.	Current amps.	Current density amps/sq.cm.	Time minutes
0·1092	1·4	5	3·5	15
0·0546	1·4	5	3·5	30
0·0273	1·4	5	3·5	45

In each case the germanium was readily detected by means of the mirror formed.

DETECTION IN THE PRESENCE OF ARSENIC.—Arsenic present in the electrolyte as an arsenate is not reduced, and the expected germanium stain is obtained.

Arsenic present as an arsenite must be oxidised as follows:—For every 0·2 grm. of arsenious oxide in 25 ml. of water add 25 ml. of concentrated nitric acid, and evaporate to dryness on a water-bath. The determination of germanium may then be made. As much as 340 mgrms. of arsenic calculated as As_2O_3 has been taken without interfering with the determination of the germanium.

THE DETERMINATION OF GERMANIUM.—Standard germanium mirrors were prepared by the electrolysis of solutions containing quantities of germanium, ranging from 0·0189 to 0·1 mgrm. These gave mirrors of increasing intensity in the combustion tube, and by comparison of the intensities of the metallic stains it was found possible to differentiate between quantities of germanium varying by 0·007 mgrm. The following additional standardisation was adopted:—Volume of solution to be electrolysed = 70 ml., made up of 10 ml. of 10 per cent. sodium hydroxide solution, germanium dioxide solution, and water to 70 ml. Area of cathode exposed to solution = 1·4 sq.cm. Current = 4 amps.

SUMMARY.—An electrolytic method for the determination of traces of germanium from 0·0189 mgrm. upwards in the presence of large quantities of arsenic has been described. The method is more sensitive than the chemical one of Müller and Smith. Experiments are being carried out at present on the latter method to investigate the possibility of its improvement, and, in particular, of its adaptability to the separation of germanium from arsenic.

I should like to take this opportunity of expressing my thanks to Dr. H. J. S. Sand, at whose suggestion this investigation was undertaken, for his interest and advice, and also to Dr. S. Judd Lewis for the germanium dioxide used in the experiments.

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Investigations into the Analytical Chemistry of Tantalum, Niobium, and their Mineral Associates

XXVI. The Interference of Tungsten in Earth-Acid Determinations

BY W. R. SCHOELLER, PH.D., AND C. JAHN

(*Work done under the Society's Analytical Investigation Scheme*)

IN an earlier paper (VIII, ANALYST, 1927, **52**, 506), we have described new methods for the separation of tungsten from tantalum and niobium. The present Section deals with the position of tungsten in our proposed scheme of mineral analysis, based upon the conversion of the earth acids and their mineral associates into soluble organic complexes. We wished to ascertain whether tungsten, as a minor constituent of the minerals under discussion, could be quantitatively recovered with, or separated from, the earth acids through the application of our precipitation methods, and thus become a member of one of the analytical groups into which the constituents may be subdivided. We have previously shown that tungsten by itself is precipitated, though incompletely, by tartaric hydrolysis (XVI, ANALYST, 1929, **54**, 704), but is not precipitated from tartrate solution by tannin or cupferron (XVII, *id*, 710, 713).

With this end in view, we treated solutions of tantalum and niobium, containing known small amounts of tungsten, as described below, and examined the weighed pentoxide precipitates for tungsten (VIII, *loc. cit.*, p. 511), which was precipitated with tannin and cinchonine (VII, *id.*, 504). The determinations proceeded very smoothly, especially after introduction of a manipulative detail consisting in the thorough mixing of a cream of filter pulp with the suspension of the tungsten-tannin precipitate prior to the addition of cinchonine reagent. By adopting this simple expedient and omitting the boiling of the liquid after adding cinchonine solution, we entirely prevented formation of a gummy precipitate adhering to the beaker. After standing overnight, the liquid was decanted through a filter, and the pulp suspension was squeezed in the beaker with a glass rod for the removal of the solution; the suspension was then stirred up with cinchonine wash-liquor.

Before proceeding to describe our tests, we feel bound to refute Moser and Blaustein's misinterpretation (*Monatsh. Chem.*, 1929, **52**, 351) of our tannin cinchonine method. Two years after its publication these authors advanced a tannin procedure based on exactly the same principle as ours, namely, complete flocculation of the colloidal tungsten-tannin complex by means of an alkaloidal reagent; with this unessential difference, that they employ antipyrin instead of cinchonine. In introducing their method they comment upon ours to this effect (reference to our paper being omitted): Schoeller and Jahn had previously ascertained that tungstic acid is incompletely precipitated by tannin, but they succeeded in precipitating the balance with cinchonine, which had been previously advocated by Cremer. This reagent, which by itself precipitates tungstic acid, renders the use of tannin really (*eigentlich*) unnecessary.

We invite reference to Section VII (*loc. cit.*), which describes how the tannin cinchonine method was evolved, cinchonine alone having given us low results in presence of much alkali chloride. The reader will then be in a position to draw his own conclusion as to the accuracy of Moser and Blaustein's interpretation of our work.

EXPERIMENTAL PART.—The mixed oxides were fused with bisulphate, and the melt was dissolved in tartaric acid or ammonium oxalate solution, as specified below. Precipitation was effected:

(*a*) By hydrochloric acid from tartaric acid solution (tartaric hydrolysis), in Exps. 1 and 2 (XVI, ANALYST, *loc. cit.*, 704).

(*b*) By tannin from neutralised tartrate solution, in Exps. 3 to 7 (XVII, *loc. cit.*, 710).

(*c*) By tannin from faintly acid oxalate solution half-saturated with ammonium chloride, in Exps. 8 to 10 (XXIII, *id.*, 1932, **57**, 552).

(*d*) By fractional precipitation with tannin from oxalate solution for the separation of tantalum from niobium, in Exps. 11 and 12 (XXIV, *id.*, 1932, **57**, 751).

(*e*) By cupferron from tartaric acid solution, in Exps. 13 to 15 (XVII, *loc. cit.*, 713).

(*f*) By cupferron from oxalate solution, in Exps. 16 and 17 (as for (*e*)).

The precipitates thus obtained were ignited, weighed, and tested for tungstic oxide (*vide supra*), with the following results (in grms.):

	Taken					
Exp.	M_2O_5	WO_3	M_2O_5 ppt.	WO_3 in ppt.	Remarks	
1	M_2O_5 0·1510	0·0148	0·1623	0·0127	$KHSO_4$, 3 grms.; $H_2\overline{T}$ 3 grms.	
2	M_2O_5 0·1507	0·0150	0·1584	0·0107	,, 4 ,, ; ,, 6 ,,	
3	none	0·0154	0·0012*	nil	* SiO_2 and Fe_2O_3.	
4	Ta_2O_5 0·2050	0·0158	0·2066	0·0026	Used 1·5 grm. tannin.	
5	Ta_2O_5 0·2006	0·0148	0·2098	0·0094	,, 2 grms. ,,	
6	Nb_2O_5 0·2041	0·0150	0·2193	0·0124	,, 2 ,, ,,	
7	Nb_2O_5 0·2047	0·0148	0·2168	0·0128	,, 2 ,, ,,	
8	none	0·0158	*	0·0016	* Small ppt. after several days.	
9	Ta_2O_5 0·2016	0·0152	0·2087	0·0078	Used 2 grms. tannin.	
10	Nb_2O_5 0·2021	0·0150	0·2162	0·0132	,, 2 ,, ,,	
11	Ta_2O_5 0·1546	0·0152	0·1538	0·0018	Ta fraction.	
	Nb_2O_5 0·1547		0·1625	0·0065	Nb fraction.	
12	Ta_2O_5 0·0528	0·0150	0·0582	0·0038	Ta fraction.	
	Nb_2O_5 0·2023		—	—	Nb fraction lost.	
13	Ta_2O_5 0·2000	0·0153	0·2111	0·0137	Ta_2O_5 recovery error	−0·0026
14	Ta_2O_5 0·2032	0·0150	0·2116	0·0118	,, ,, ,,	−0·0034
15	Nb_2O_5 0·2037	0·0158	0·2080	0·0049	Nb_2O_5 ,, ,,	−0·0006
16	Ta_2O_5 0·2018	0·0150	0·2122	0·0126	Ta_2O_5	−0·0022
17	Nb_2O_5 0·2009	0·0158	0·2045	0·0041	Nb_2O_5 ,,	−0·0005

CONCLUSIONS.—A glance at the Table shows that none of the procedures used achieves a complete precipitation of tungsten with the earth acids or its complete separation therefrom, but, instead, it distributes itself over the precipitates and filtrates. Hence, tungsten as a constituent of earth-acid minerals calls for a new procedure aiming at its complete separation from the earth acids, as well as from associated dioxide earths and other earths. With the help of our collaborator, Mr. A. R. Powell, we have succeeded in working out such a procedure by applying the principle of Bedford's method for the separation of tungsten from niobium, *viz.* the action of magnesia mixture on alkaline solutions of the metallic acids (ANALYST, 1927, **52**, 510). The process will be described in a forthcoming Section.

Several other conclusions and observations of analytical interest were obtained as the result of the above experiments:

(*a*) In tartaric hydrolysis, the earth acids induce precipitation of subordinate amounts of tungstic acid to a marked degree, though the tungsten precipitation is not quantitative.

(*b*) In all the tannin precipitation tests, niobium induces more pronounced tungsten precipitation than does tantalum.

(*c*) In Exp. 9 the co-precipitated tungsten discoloured the tantalum precipitate, to which it imparted a pale brown tinge. The same discoloration could not be observed in Exps. 4 and 5, since tantalum precipitates produced in neutralised tartrate solutions are invariably bleached by traces of co-precipitated iron (XIX, *id.*, 1931, **56**, 307, *D*).

(*d*) In the separation of tantalum from niobium a subordinate amount of tungsten, besides contaminating the earth-acid fractions, renders the fractionation less readily observed by reason of the slight brownish tinge of the tantalum precipitates; this may not appear at once, but only after a few minutes. The interference of tungsten is similar to, but less pronounced than, that of small amounts of titania (XI, *id.*, 1928, 53, 264). It is more pronounced with low Ta:W ratios (Exp. 12); the filtrates may show a brownish-yellow tint.

(*e, f*) Like tannin, cupferron does not precipitate tungsten by itself, but partial precipitation is induced by the earth acids. We used 50 ml. of a 6 per cent. solution of the reagent in each test. The tantalum precipitates were crystalline in appearance; the niobium precipitates were plastic and adhesive, addition of filter pulp improving the filtration. In cupferron precipitations it is tantalum, not niobium, that induces more extensive tungsten precipitation; but the niobium recovery is more complete than that of tantalum, minute quantities of which were detected in the cupferron filtrates (XIX, *loc. cit.*, 310, *G*).

The above findings confirm an observation in Hillebrand and Lundell's *Applied Inorganic Analysis* (New York, 1929, 110, footnote) to the effect that, in separations by means of cupferron, "tungsten is partially precipitated no matter how much sulphuric and tartaric acids are used."

From what precedes, it appears to us that tungsten is the most troublesome minor constituent with which we have to deal in the analysis of earth-acid minerals.

SUMMARY.—When the earth acids are precipitated by tartaric hydrolysis, the co-precipitation of subordinate amounts of tungstic acid is incomplete. Neither tannin nor cupferron precipitates tungsten by itself from tartrate or oxalate solutions, but preponderating quantities of earth acid induce partial precipitation of tungsten. On account of its incomplete precipitation in all these procedures, we cannot yet assign to tungsten a definite position in our proposed analytical scheme. What we require is an additional method for the separation of tungsten from the earth acids as well as from other associated earths. A method to that end will shortly be published.

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The Use of the Air-Damped Balance for the Determination of Total Solids in Milk

BY J. GOLDING, D.S.O., F.I.C.

(*Read at the Meeting, December* 6, 1933)

THIS paper should be regarded as only a preliminary communication, for, while the work was in progress with an air-damped balance of foreign manufacture, a new and even more sensitive air-damped, prismatic reflecting balance of British make has still further encouraged developments in the use of this type of balance for analytical operations.

Nevertheless, my experience with this new balance is limited to my own conditions, in which vibration is reduced to a minimum, and the extreme sensitiveness of the balance is an advantage. In my own case, my modifications in technique have removed difficulties and enabled me to meet requirements for a large number of determinations of total solids in milk, without increased laboratory accommodation or assistance for the work.

These difficulties have been overcome by the use of three new types of apparatus:—The first was an air-damped balance, which has greatly shortened the time and labour of weighing. The second was the use of small aluminium milk-bottle caps, which I adopted in place of large nickel dishes previously used, thus saving space and expense. The third was the adaptation of a syringe for measuring the milk before weighing—also a time-saving convenience.

The first air-damped balance used was a Kaiser and Siever balance, which has an illuminated scale on which a decigram and fractions of a decigram are shown; the open scale is divided into mgrms. The balance comes to rest in 15 to 20 seconds. The only weights required are the grams and decigrams, and this again saves time. Forty dishes containing total solids have been weighed on this balance, each to 0·2 mgrm., in 30 minutes. The tenths of a milligram are estimated, but the error should not exceed 0·0002 grm. at most.

I have recently obtained a still more sensitive air-damped prismatic reflecting balance by Oertling, having only one air-damping chamber. This has a very highly magnified, illuminated scale, graduated and marked up to 500 tenths of a milligram; no weights below 0·05 grm. are therefore used on the pan. With this balance it is possible to weigh to 0·05 mgrm. The balance, however, needs careful adjustment, and does not come to rest so quickly as the Kaiser and Siever balance. Thirty dishes containing total solids have been weighed on the Oertling balance to four places of decimals in 30 minutes.

Here 0·1 mgrm. is a reliable figure, but I do not attempt to use the fifth place of decimals, although the scale would admit of weighings to a greater accuracy than 0·1 mgrm. Both balances require a very firm support; I use brick piers specially built, but a wall bracket has served well with the Oertling balance.

The cost, a drawback to the air-damped balances, cannot be urged against the aluminium dishes or bottle caps, which are only 10s. 6d. per 1000. They are 44 mm. in diameter, 7·4 mm. deep, and 0·18 mm. thick, and vary in weight only from 1·1 to 1·3 grm. Before use the caps are rinsed with alcohol, followed by a fat solvent (Röse-Gottlieb distillates), to remove a trace of lubricant used in their manufacture; they lose only about 1 mgrm. by this treatment. They are easily cleaned and can be used again and again. They alter very little in weight if carefully cleaned and freed from traces of fat by means of alcohol and ether.

The great advantages of these small dishes are that they do not alter in weight while being weighed, and that they take up so small a space in ovens and desiccators. Our oven, which measures 14½ by 14¾ by 15½ inches, is fitted with five staggered copper trays. A supply of heated air is admitted at the four corners of the floor of the oven through four metal tubes. The intake of external cold air to these tubes is at the opposite side to that on which it is admitted into the oven. Each tube passes through the boiling water in the detachable water-bath under the oven, and the air is thus heated before it passes over the staggered trays. The oven door should fit tightly, and it is probable that the slightly higher results which were later obtained when milks were dried in front positions on the shelves, compared with those dried in back positions (see below), were due to a draught of cold air under our oven door. The oven will hold 245 dishes at one time.

Our technique for total solids consists in weighing the clean, dry dishes as taken from a desiccator, and, while they are still on the balance pan, introducing a syringe-full of well-mixed milk quickly into each dish, which is then weighed again. The syringe is adjusted to deliver just over 1 grm. of milk, which it does with great rapidity, and with a variation of not more than 3 mgrms. After delivering each sample it is quickly cleaned by rinsing it out with two or three fillings of milk. The weighed caps of milk are placed in rows on one of the copper trays, which is covered with a sheet of glass. When a batch of milks, up to 49, has been weighed out, the glass plate is removed and the tray is placed over a steam-bath for 15 minutes. After the milk has evaporated the tray is wiped underneath and slid into the oven.

After two to three hours, when the milks are dry, the dishes containing the solids are placed in desiccators holding 10 dishes each, cooled for 5 minutes, and weighed; a second weighing is taken after another hour in the oven. This reduces the handling of individual dishes to a minimum.

The results given in Table I indicate that the most concordant results are obtained after two to four hours' drying, and that further periods, even of 7 hours, in the oven give a slightly lower, but still closely agreeing, figure. Table I also shows the close agreement between 25 determinations made on the same bulk of milk, even though divided into four samples and weighed after different intervals in the oven.

Although a further loss of 0·001 to 0·05 per cent. may be obtained by further heating for 7 hours in the oven, the steady figure obtained after 2 to 4 hours is taken as correct. The old method of drying 5 grms. in a flat nickel dish, 3½ inches in diameter, gave slightly higher results.

For comparison, 44 pairs of determinations were carried out by the original method and by the new method with the Kaiser and Siever balance, side by side. The difference between the new and old methods worked out at —0·021 per cent., *i.e.* the old method gave a slightly higher result. The standard error of difference was ±0·0064.

The results available for a comparison of the methods are shown in Figs. 1, 2, and 3.

Figs. 2 and 3 are not strictly comparable with Fig. 1, as only 600 pairs of duplicate analyses have at present been made by the new method: 300 on each balance.

In each case the columns indicate the percentage of differences falling into the following groups:—

0=0—0·005 per cent., 0·01=·006 to ·015 per cent., 0·02=0·016 to 0·025 per cent., 0·03=0·026 to 0·035 per cent., and so on.

The average differences are given under each column, and also the number in each group per 100 duplicate determinations.*

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* If the percentage of total solids in the milk be regarded as the number of grms. of solids in 100 grms. of milk, then the unit of this figure may be regarded as grms. The expression percentage has been avoided in describing this and similar values because of possible ambiguity in its meaning.

Fig. 1 shows the percentage distribution of differences obtained between duplicate determinations of total solids in 3461 samples of mixed milk from our typical herd tested between October 1st, 1928, and July, 1933. The figure indicates that small groups of differences tail out to a very unsatisfactory extent. The greatest difference between duplicates was 0·3 per cent., which was the difference between one pair of results in 3461 samples. About 98·5 per cent. of the samples

PER 100 DUPLICATE DETERMINATIONS

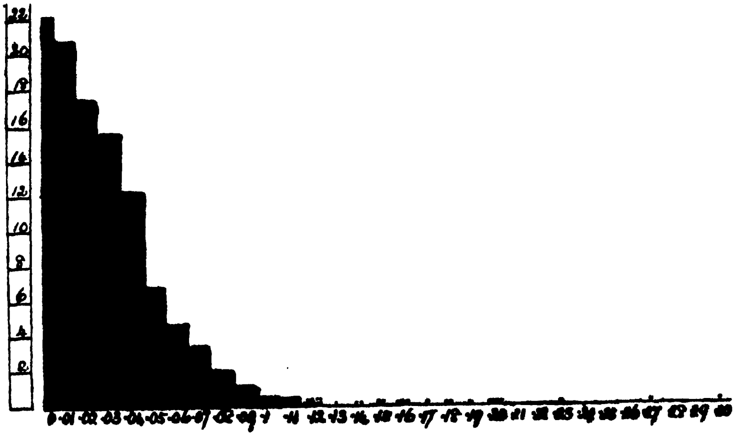

Fig 1. Old Method

Showing differences between duplicate determinations of the percentage of total solids in 3461 samples. Each dot (·) shows an error of the magnitude indicated in all the 3461 duplicate determinations

GROUP OF DIFFERENCES PER 100 DUPLICATE DETERMINATIONS

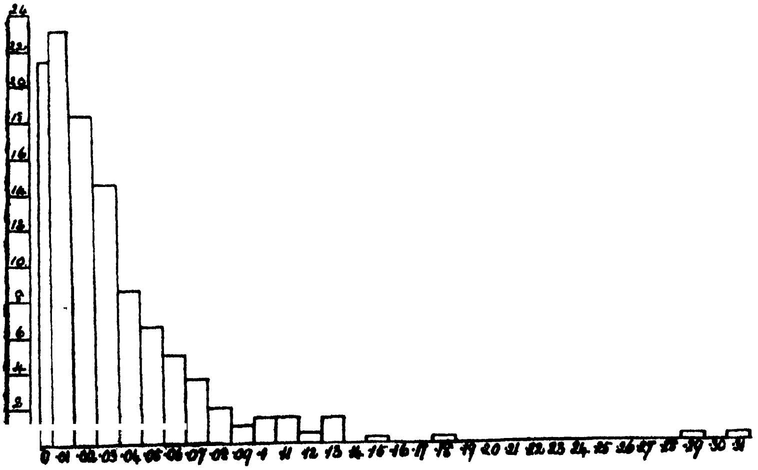

Fig. 2

Showing differences between duplicate determinations of the percentage of total solids in 300 samples. One grm. of milk used with air-damped balance weighing to 0·2 mgrm.

agreed within 0·1 per cent. of total solids, but the remainder were outside this range. Unfortunately, the cause of these occasional errors was not investigated at the time, but some tangible sources of error are indicated, and these provide another reason for revision of our old method. They were all made by the old method, in which about 5 grms. of milk was weighed into flat nickel dishes, 3½ inches in diameter,* and with the use of an ordinary analytical balance weighing to 1 mgrm. The standard difference is 0·04 grm., and the standard error of a single determination ±0·028 grm.

Fig. 2 shows the percentage distribution of differences obtained between duplicate determinations of total solids in 300 samples of milk, about 1 grm. of milk being weighed in aluminium on the Kaiser and Siever balance, with an accuracy of 0·2 mgrm. The duplicate determinations were not made side by side, and were sometimes left until the following day. Even so, the standard difference is 0·05 grm., which makes the standard error of a single determination ±0·035 grm. In this case, although the speed was much greater, the accuracy is less than with the older and slower method.

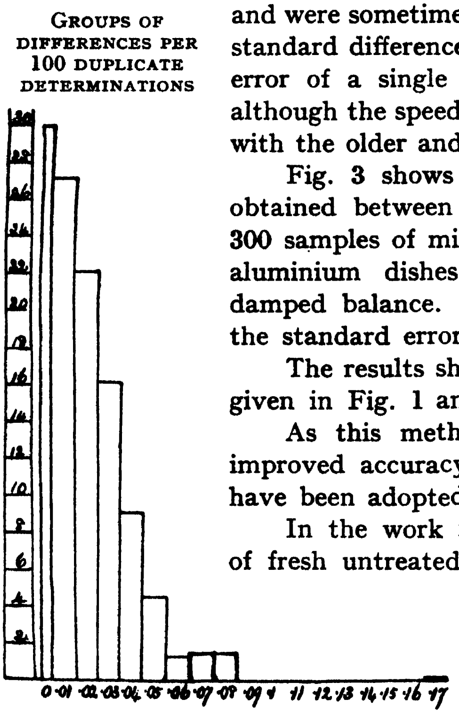

Fig. 3

Showing differences between duplicate determinations of total solids in 300 samples. One grm. of milk used with air-damped balance weighing to 0·1 mgrm.

Fig. 3 shows the percentage distribution of differences obtained between duplicate determinations of total solids in 300 samples of milk, about 1 grm. of milk being weighed in aluminium dishes to 0·1 mgrm. on the new Oertling air-damped balance. The standard difference is 0·03 grm., and the standard error of a single determination ±0·021 grm.

The results show an improvement in accuracy over those given in Fig. 1 and Fig. 2.

As this method and technique give increased speed, improved accuracy, and economy of space and labour, they have been adopted.

In the work reported above, all the samples used were of fresh untreated milk. For such milk 1 grm. is the most convenient quantity to take.

In addition to those discussed above, nine series of 25 determinations each have been made on nine separate samples of milk. In each series the 25 dishes were distributed in 25 recorded positions in the ovens, with the object of finding out if the position in the oven contributed to slight differences of result which still persisted. All the results agreed well, and the differences were of the same order as those shown in Fig. 3. The standard error of a single determination was 0·022.

There appeared to be no significant difference between the different shelves. However, the samples dried in the front positions on the shelves showed a significantly higher value than those dried at the back of the shelves.

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* These can be obtained from Messrs. Alka, Ltd., Alka Works, Minerva Road, North Acton, N.W.10.

TABLE I

Total solids per cent. in four samples taken from one sample of mixed milk, showing the influence of the time of drying. Percentage calculated on each weighing of 1·015 to 1·0178 grms. of milk taken in 25 aluminium caps and weighed on an Oertling air-damped prismatic reflecting balance.*

Weighed at half-hour intervals and finally after 2 and 7 hours

	Sample					
Successive times in oven	I	II	III	IV	I	Average
½ hour	11·932	11·910	11·927	11·949	11·916	11·926
½ hour	11·892	11·880	11·897	11·910	11·887	11·893
½ hour	11·863	11·841	11·838	11·841	11·828	11·842
½ hour	11·843	11·821	11·848	11·861	11·828	11·840
½ hour	11·853	11·831	11·848	11·851	11·828	11·842
½ hour	11·843	11·841	11·838	11·831	11·828	11·836
2 hours	11·823	11·801	11·809	11·812	11·798	11·808
7 hours	11·813	11·801	11·819	11·812	11·789	11·806
Weighed at 1-hour intervals						
	I	II	III	IV	II	
1 hour	11·931	11·899	11·920	11·880	11·904	11·906
1 hour	11·881	11·860	11·881	11·851	11·865	11·867
1 hour	11·871	11·830	11·861	11·831	11·845	11·847
1 hour	11·871	11·840	11·852	11·831	11·835	11·845
1 hour	11·841	11·820	11·842	11·812	11·835	11·830
1 hour	11·842	11·830	11·852	11·821	11·835	11·836
7 hours	11·832	11·820	11·842	11·802	11·826	11·824
Weighed at 2-hour intervals						
	I	II	III	IV	III	
2 hours	11·837	11·855	11·843	11·822	11·856	11·842
2 hours	11·847	11·845	11·833	11·822	11·856	11·840
2 hours	11·847	11·835	11·813	11·832	11·837	11·832
7 hours	11·827	11·826	11·813	11·842	11·827	11·827
Weighed at 3-hour intervals						
	I	II	III	IV	IV	
3 hours	11·869	11·865	11·848	11·847	11·830	11·851
3 hours	11·859	11·865	11·848	11·827	11·820	11·843
7 hours	11·839	11·856	11·839	11·827	11·820	11·836
Weighed at 4-hour intervals						
	I	II	III	IV	I	
4 hours	11·868	11·863	11·854	11·835	11·841	11·852
4 hours	11·829	11·843	11·824	11·815	11·821	11·826
7 hours	11·809	11·843	11·844	11·835	11·831	11·832

* The third place of decimals is only an estimate; it is retained to indicate the nearest 1/10th milligram between successive weighings at intervals of time given in the margin.

The Roman numerals give the numbers allotted to the four sub-samples. The agreement between these indicates effective mixing.

The averages of 5 determinations after each successive period in the oven are given as percentages of total solids in the last column.

Of the deviations from the mean of all the determination, 76 per cent. of those which exceeded the mean by more than 0·015 per cent. were dried in front positions on the shelves.

By avoiding the use of the front positions on the shelves and packing the door of the oven, the standard error of a single determination may be reduced below 0·02.

With the object of avoiding frequent adjustments of the zero-point to obtain weighings of the total solids to 0·0001 grm., a second air-damping chamber is being added; this is expected to eliminate this difficulty.

In conclusion, my thanks are due to "Student," to Mr. L. McMullen and to Dr. S. Bartlett for statistical criticism, and to Mr. A. Wagstaff, who carried out most of the analyses.

THE NATIONAL INSTITUTE FOR RESEARCH IN DAIRYING
SHINFIELD, NEAR READING

Vitamin *D* in Cacao Shell

BY ARTHUR W. KNAPP, M.SC., F.I.C., AND KATHARINE H. COWARD, D.SC.

CACAO seeds or "beans" consist of 87·3 per cent. of nibs (*i.e.* broken cotyledons), 0·7 per cent. of germ (radicle) and 12 per cent. of shell or husk (the spermoderm with adhering parts of pericarp and perisperm). The nib is the part used by the cocoa and chocolate manufacturer, and the shell is a by-product which is used in cattle food.

In 1928 milk chocolate of known composition was subjected by us to feeding tests for vitamin assay. The number of units of vitamin *D* found was greater than could be accounted for solely by the concentration of the milk, and, as the only other ingredients were sugar and cacao bean nib, it became evident that the cacao-bean nib must supply the remainder of the vitamin *D*.

As a result of this observation in 1928, we tested biologically a sample of nib prepared from Gold Coast cacao and confirmed the presence of vitamin *D*, the amount present being one unit of anti-rachitic activity per grm. of nib (see *J. Soc. Chem. Ind.*, 1932, 1008). The nib tested was free from shell, but contained the germ or radicle. Only a small amount of vitamin *A* was found, and no vitamin *B*. Other investigators have found vitamin *B*; Sasika and Wakayama (*J. Agr. Chem. Soc., Japan*, 1932, **8**, 160; C.A., 1932, **26**, 5326) have reported the presence of anti-neuritic vitamin *B* in cacao beans, and Labbé, de Balsac and Lerat (*Bull. Soc. Therap.*, 1931, 12, 36, 175; C.A., 1932, **26**, 2770) have found vitamin *B* in the cacao germ. The latter authors have also shown that cacao butter contains a small quantity of vitamin *A* (*Bull. Soc. Therap.*, 1930; *B.C.A.*, 1931, A, 988).

Our discovery of vitamin *D* in cacao nib caused us to consider how it had originated. We know that during the preparation of cacao beans for the market, that is during fermentation and subsequent drying, there is a passage outwards of various constituents of the nib (*e.g.* theobromine, tannin, and other substances at present unidentified into the shell (Knapp and Wadsworth, *J. Chem. Soc. Ind.*, 1924, 124T), and also, on the other hand, that the acids in the pulp on the outside of the shell pass inwards into the nib. The final constituents of the shell and nib are, therefore, closely interdependent. We know that both contain fat, and that the small quantity of fat in the shell is not markedly different from that in the nib. Our discovery of vitamin *D* in nibs led us to expect vitamin *D* in shell, and, since the seeds are exposed to the tropical sun for a number of days, it was reasonable to expect the shell to be appreciably richer than the nib in vitamin *D*.

Observations by Labbé, de Balsac, and Lerat (*Comp. rend.*, 1929, **189**, 864; *B.C.A.*, 1930, 121*A*) encouraged this expectation. They found in cacao two sterols, and these, particularly the α-theosterol, when treated with ultra-violet light, cured rickets. They noted that the shell was richer in these sterols than either germ or nib. They found 6 to 8 per cent. of sterols in the fat from the shell, as compared with 0·3 to 0·4 per cent. in the fat from the nibs.

For the purpose of testing for vitamin *D*, a sample of cacao shell was obtained in the factory from a full-sized commercial plant, so as to be representative of ordinary cacao shell. Shell from Gold Coast beans was selected for the test, as West Africa is responsible for more than half the world's cacao production. Most of the cacao produced on the Gold Coast undergoes fermentation. There is little or no artificial drying, the cacao being dried by turning over and over in the sun, a process which usually takes at least six days.

The beans were ordinary Gold Coast cacao, the grade known commercially as "good fermented" or Grade 1, and in this case actually contained about 98 per cent. of fermented beans and 2 per cent. of unfermented beans. The beans were passed through the cleaning plant and roasted, broken and winnowed in the ordinary way. The fraction consisting of large fragments of shell was taken. This contained only traces of nib or germ. The shell was ground to a fine powder to make it more suitable for feeding to rats.

The biological tests were carried out under the direction of one of us (K. H. C.) at the Pharmacological Laboratories of the Pharmaceutical Society. They consisted of an estimation of the vitamin-*D* content of the powdered cacao-bean shell in terms of the International Standard for vitamin *D*. The method of estimation was the one usual in those laboratories. Young rats weighing about 60 grms. were made rachitic by feeding them on a rickets-producing diet (Steenbock's 2965) for 3½ weeks. Half the rats of each litter used were given a single dose of irradiated ergosterol, the International Standard, at the beginning of the ten days' curative period, while the cacao-bean shell was given as a percentage of the diet of other rats throughout the ten days' curative period (in the first experiments) or as a small dose directly into the rat's mouth, 0·05 grm. on each of the first 5 days and none on the last 5 days of the curative period (second experiment). In the first experiment, the cacao-bean shell had been given as 1, 10 and 20 per cent. of the diet, respectively, one litter of rats being used to compare each of these quantities with a total dose of 5 units of vitamin *D*. Records of the amount of food eaten by each rat were made each day, and from these records the total amounts of cacao-bean shell eaten during the test were calculated.

At the end of the 10 days' curative period the rats were killed, the distal ends of the radii and ulnae were placed in 4 per cent. formaldehyde for a few days, then separated with a sharp scalpel, cut longitudinally, and stained by placing in 1·5 per cent. silver nitrate solution and exposing to sunlight. The calcified parts of the bones blackened, and it was thus possible to compare the healing produced in the different bones by the cacao-bean shell and by the standard vitamin *D*.

The healing in each bone was assessed by comparison with a series of bones showing graded amounts of healing given values 0 to 6. The ratio between the average amount of healing shown by a number of rats all given a certain dose of cacao-bean shell and that shown by other rats given a dose of the standard is not the ratio of the potencies of the doses. The ratio of healing is converted into the ratio of the potencies of the doses by finding the abscissae corresponding with these average amounts of healing from the curve of response relating healing to dose of vitamin *D* given.

The results of the first experiment with the cacao-bean shell may be seen in Table I.

TABLE I

Total dose	Litter	Rat	Healing
0·85 grm. C.S.	2742	5431	3·0
0·82 grm. C.S.		5432	4·0
5 units *D*.		5430	1·0
5 units *D*.		5433	2·0
9·5 grms. C.S.	2741	5426	6·0
7·9 grms. C.S.		5428	5·0
5·6 grms. C.S.		5429	6·0
5 units *D*.		5424	1·0
5 units *D*.		5425	1·5
5 units *D*.		5427	1·5
No dose	2744	5443	0
20·2 grms. C.S.		5440	6·0
19·4 grms. C.S.		5444	5·0
17·8 grms. C.S.		5446	5·0
5 units *D*.		5441	1·5
5 units *D*.		5442	2·0
5 units *D*.		5445	1·5

It was evident that the cacao-bean shell was much richer in vitamin *D* than had been anticipated. The first litter, *i.e.* the one on which the smallest amount of cacao-bean shell was tested, was the only one from which any calculation of the

TABLE II

Dose	Litter	Rat	Healing	Average Healing
No dose	2774	5599	0	0
0·25 grm. cacao-bean shell	2774	5598	2	
		5603	3	
		5604	1·5	2·4
	2775	5606	3	
		5608	2	
5 units *D*.	2774	5600	1	
		5601	3	
		5602	2·0	1·9
	2775	5605	2	
		5607	1	

CACAO-BEAN SHELL TESTS

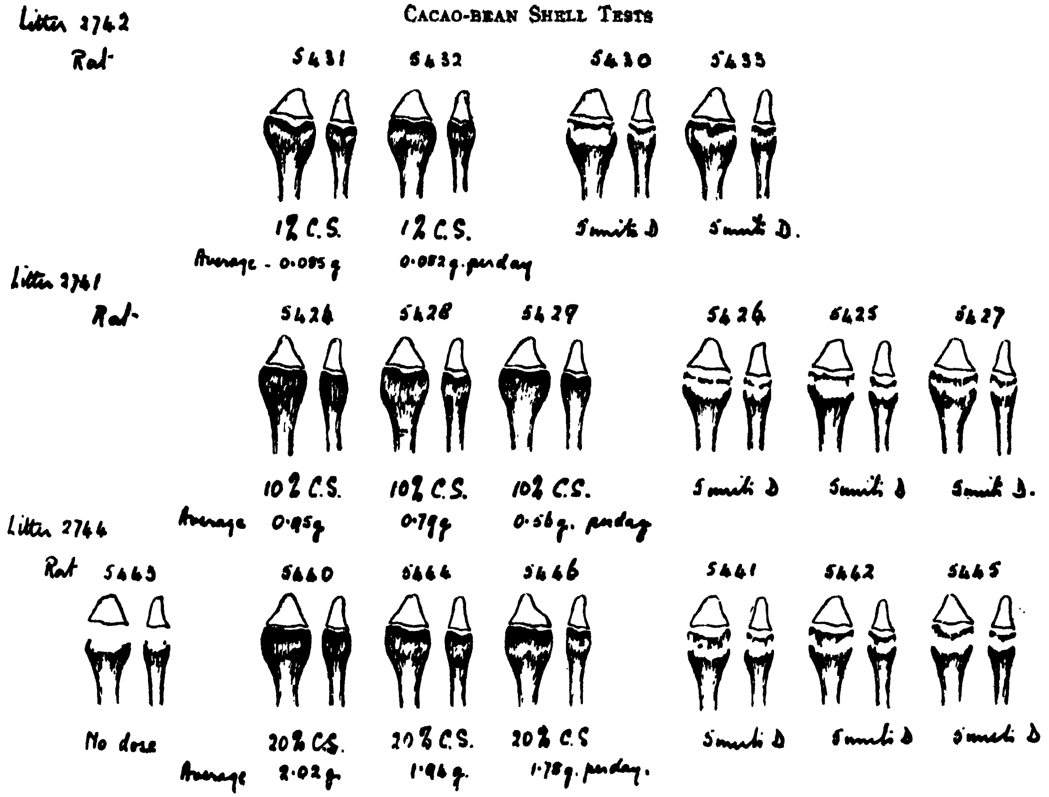

Fig. 1 (illustrating Table I)

The whole of the dose of Standard D was given on the first day of the test

CACAO-BEAN SHELL TESTS

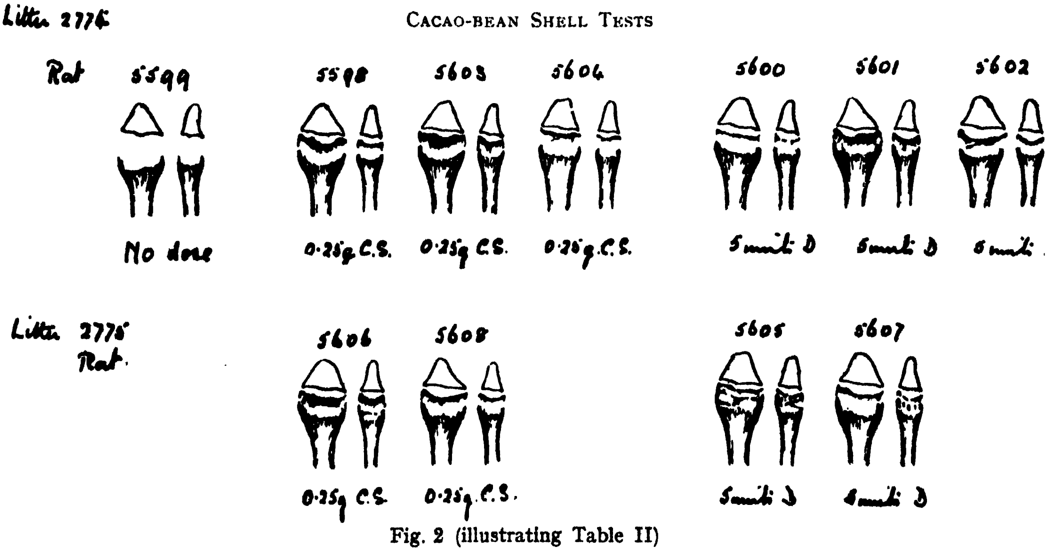

Fig. 2 (illustrating Table II)

Drawings of the calcified parts (only) of a radius and ulna from each rat used in the tests. A severe rachitic condition was produced in each rat as judged by the width of the metaphyses. The degree of healing produced by the cacao-bean shell was judged by the amount of calcification produced in the metaphyses of each rat.

potency could be made; in the other litters the healing brought about by the cacao-bean shell was too great for an accurate calculation. The first litter gave a value of 25 units of vitamin *D* per grm. of powdered cacao-bean shell, but, as only 4 rats had been used in this comparison, another test was made. A smaller dose of cacao-bean shell, 0·25 grm. altogether (5 doses of 0·05 grm.) was compared with 5 units of vitamin *D*. The result may be seen in Table II.

In this test the average healing of the rats given 0·25 grm. of cacao-bean shell was 2·4, and that of the rats given 5 units of vitamin *D* was 1·9. The abscissae corresponding with these averages of the curve of response relating average healing to dose of vitamin *D* were 0·18 and 0·13, respectively. Thus the vitamin *D* content of 0·25 grm. of cacao-bean shell is $\frac{0{\cdot}18}{0{\cdot}13} \times 5$ units $= 7$ units. Therefore, the vitamin *D* potency of the cacao-bean shell is estimated from this test as 28 units per grm. This result confirms the earlier ones, and it may safely be concluded that the sample of cacao-bean shell contains about 28 units of vitamin *D* per grm.

This potency in vitamin *D* is high for any product, and may be compared with a figure of 100 units per grm. which is given by an average sample of cod-liver oil. For a vegetable product the figure is quite exceptional. It raises the general question whether vitamin *D* is produced by exposure to the sun during the drying of other fat-containing products, *e.g.* copra, coffee, spice, oil-bearing seeds, nuts, etc. Dann (*Biochem. J.*, 1932, **26**, 151) has shown that native-produced palm oil has a potency of about 1/30th that of cod-liver oil, which is higher than that of plantation palm oils, presumably because it has been exposed to the tropical sun for long periods. One of us (K. H. C.) has already reported (*Lancet*, 1933, 930) the anti-rachitic activation of yeast by exposure to strong sunlight. It is worth noting that yeasts can always be found on the shells of fermented cacao-beans.

Manufacturers have often stated that they prefer sun-dried cacao to that dried artificially. One of the desirable changes in cacao beans is oxidation of the tannins, which takes place during sun-drying. In artificial drying, temperatures over 75° C. are liable to be reached, and this destroys the enzyme essential to oxidation. Not only does the sun's heat provide a suitable temperature but, according to recent work by Steinmann (*Z. Unters. Lebensm.*, 1933, **65**, 454), exposure to sunlight actually liberates cacao red which, in the presence of oxidase, is oxidised to cacao brown. A further possible advantage of sun-drying is that this may result in a higher vitamin *D* content in cacao shell, and possibly in nib.

The shell of the raw, fermented cacao bean contains 1 to 2 per cent. of a rather acid fat. During roasting a little of the cacao butter from the nib is absorbed by the shell, so that it is usual to find in the roasted cacao shell at least 3 per cent. of substances extractable with petroleum spirit. This extract is mainly fat, and if, as seems possible, the whole of the vitamin *D* is concentrated in it, it must have a very high potency.

SUMMARY.—A sample of shell from fermented sun-dried Gold Coast cacao was found to be rich in vitamin *D*. It contained 28 units of vitamin *D* per grm.

Notes

The Editor wishes to point out that the pages of the Journal are open for the inclusion of short notes dealing with analytical practice and kindred matters. Such notes are submitted to the Publication Committee in the usual manner.

THE PREPARATION OF IODINE-FREE POTASSIUM HYDROXIDE

For the determination of the very minute quantities of iodine present in milk and other foods it is necessary to add relatively very large quantities of potassium hydroxide. This reagent, if of ordinary A.R. quality, frequently contains sufficient iodine to raise the value of the "blank" determination to a figure of the same order as that found in the actual analysis, and no very satisfactory method of purifying the reagent appears to have been placed on record.

A satisfactory electrolytic method of purification has been used for some time in the Government Laboratory, but this method is somewhat complicated, and it was realised that a simpler method would be welcomed by the various laboratories interested in work of this nature.

Von Fellenberg's method for the preparation of iodine-free potassium carbonate depends on the distribution of potassium iodide between a saturated solution of potassium carbonate and a solution of ethyl alcohol, the iodide being quantitatively extracted by the alcohol, but this method is not applicable to the purification of potassium hydroxide. Perusal of a recent paper by Gibby (*J. Chem. Soc.*, 1934, 9), on the system acetone—potassium hydroxide—water, indicated that an investigation of the distribution of minute quantities of potassium iodide between acetone and a saturated solution of potassium hydroxide might be of interest.

Accordingly, the removal of 4·0γ of added potassium iodide from a saturated aqueous solution of potassium hydroxide was examined, the aqueous solution being repeatedly extracted by shaking with an equal volume of acetone, and the acetone layers being examined separately for iodine. The results were as follows:

Recovery of 4·0γ of Potassium Iodide by Extraction with Acetone

		γ
1st acetone layer contained		1·75
2nd		1·27
3rd		0·53
4th		0·40
5th		0·16
6th	less than	0·1
Total		4·11γ

It appeared, therefore, that a new method of preparing iodine-free potassium hydroxide was available, provided that iodate, as well as iodide, could be dealt with in a satisfactory manner.

The method was finally tested by preparing a batch of iodine-free potassium hydroxide from a saturated solution to which had been added iodate and iodide in equal proportions, and in such quantities as to produce a "blank" of 2·0γ of iodine. A "blank" determination, carried out with this solution, after purification in the manner to be described, gave 0·12γ, indicating that the method of purification is efficient.

The details of the method are as follows:—The potassium hydroxide (125 grms.) is dissolved in sufficient distilled water to produce a saturated solution, and, after the addition of 0·25 grm. of hydrazine sulphate, the solution is boiled gently in a flask for about 30 minutes. After cooling, the solution is transferred to a separating funnel and extracted by shaking with an equal volume of iodine-free acetone (redistilled after addition of a little potassium hydroxide). The acetone layer is rejected, and the extraction with acetone is repeated 9 times (*i.e.* ten extractions in all, with acetone).

Finally, the aqueous solution of potassium hydroxide is boiled gently to remove traces of acetone, cooled, adjusted to 10 *N*, and, if necessary, filtered through a Whatman (No. 54) filter paper.

I wish to thank Sir Robert Robertson, the Government Chemist, for granting permission for the publication of this note.

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C. O. HARVEY

NOTE ON AN ATTEMPTED ADSORPTION INDICATOR METHOD FOR THE DETERMINATION OF ALKALI SALTS OF ORGANIC ACIDS

IT seemed desirable to investigate volumetric methods for the estimation of the alkali salts of organic acids by reactions involving the precipitation of less soluble salts. Although the search for a suitable adsorption indicator has not proved successful, the results obtained may be of interest.

The following dyestuffs have been tried as adsorption indicators for titrations, in neutral solution, of silver nitrate (*N*/5 and *N*/10) with sodium and potassium tartrate, sodium benzoate, and sodium salicylate, and for titrations, in neutral solution, of barium chloride (*M*/4) with sodium and potassium tartrate, and sodium citrate:—Afghan yellow, brilliant yellow, bromthymol blue, Chicago orange G, chloramine orange G, chlorazol fast orange AG, chlorazol fast orange R, chlorazol fast yellow, chlorophenine orange RR, chrysophenine, curucuphenine, di-iodo fluorescein, diphenyl fast yellow, eosin, fluorescein, malachite green, methyl red, phenol red, pyrazole orange R, rhodamine 6G, safranine, tartrazine, tetrabromo-tetrachlorofluorescein.

The following method of titration was adopted:—A measured volume of the silver nitrate or barium chloride solution was introduced into a glass-stoppered bottle, and the indicator was added, and then the solution of the organic salt in a quantity calculated to be slightly less than that required for complete precipitation. In another bottle a similar volume of silver nitrate or barium chloride solution was mixed with the indicator and a quantity of organic salt solution slightly greater than that required for complete precipitation. The solution in one bottle thus contained excess of barium or silver ions, whilst the solution in the other bottle contained excess of organic acid ions. The bottles were shaken to coagulate the precipitates, which were allowed to settle, and the bottles were then compared to ascertain if the precipitates or solutions showed any difference in colour. The results were confirmed by further titrations of mixtures in which the organic salt solution had been placed in the bottles first.

In general, it was found that any one dyestuff behaved similarly for all the titrations mentioned, the dyestuff being either adsorbed on to the precipitate under all conditions, or remaining always in the solution. An interesting generalisation was deduced, namely, that dyestuffs of the di-stilbene type are always adsorbed on to the precipitate, whilst the simpler mono-stilbene derivatives always remain in the solution. It will be seen from the list of dyestuffs given above, that attempts were made to find a dyestuff of an intermediate behaviour, but these attempts were not successful.

We are indebted to Messrs. The Clayton Aniline Co., Ltd., The Geigy Colour Co., Ltd., and Imperial Chemical Industries, Ltd., for gifts of some of the dyestuffs investigated.

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SOME BARIUM VALUES OF THE BUTTER-FATS OF DIFFERENT ANIMALS

THE accompanying table gives the barium-soluble and insoluble values of some butter-fats from different sources. The method employed was a volumetric one, involving the precipitation, in the cold, of the barium salts by a known volume of standard barium chloride solution, and titration of the excess of barium in the filtrate with standard potassium palmitate solution.

About 2 grms. of fat were saponified in the usual way and neutralised to phenolphthalein. The cooled solution was made up to 100 ml. with water, and 25 ml. (equivalent to 0·5 grm. of fat) were pipetted into a wide-necked 100-ml. flask to permit of vigorous shaking after bulking. The solution was diluted to about 70 ml. with distilled water, and 0·1 *N* barium chloride solution was run down the side into the flask, in amount equal to the titration value of the fatty acids in the flask, as calculated from the saponification determination.

Butter	Saponification value	Insoluble barium value	Soluble barium value	Volatile acids × $\frac{5 \cdot 6}{5}$	Difference (= soluble barium value minus volatile acids)
Goats' butter.. ..	—	180	—	31	—
	235	180	55	31	24
	229	179	50	31	19
Syrian samna ..	240	179	61	40	21
Hedjaz ,, ..	234	180	54	39	15
Iraq ,, ..	242	180	62	42	20
Sheeps' butter (Egyptian)	226	176	50	—	—
Cows' butter—					
Australian ..	229	181	48	36	12
	226	177	49	33	16
	228	181	47	33	15
Egyptian ..	229	181	48	33	16
	224	182	42	30	14
Gamoos' butter ..	226	180	46	36	10
	224	181	43	33	10
	226	176	50	36	14
	234	179	55	44	11
	234	178	56	43	13
	229	180	49	38	11
	232	181	51	38	13
	226	181	45	35	10
	226	180	46	37	9
	222	179	43	30	13
Indian "butter" ..	228	179	49	39	10
Coconut oil	259	213	46	—	—
Animal fat	196	190	6	—	—

The solution, before shaking, was made up to 100 ml., and then shaken vigorously for about 1 minute. Coagulation of the precipitate was rapid, except when the excess of barium over the insoluble acids was low, as with animal fat or vegetable oils. Under those conditions it was preferable to add a definite excess of barium, say about 5 ml., of 0·1 *N* solution more than the titration value of the acids.

The solution was filtered through a dry folded filter paper, the first 20 ml. or so being rejected, and 50 ml. of the clear filtrate were then transferred to an

Erlenmeyer flask and diluted with an equal quantity of water, and the barium was titrated with a 0·05 N solution of potassium palmitate in 85 per cent. alcohol, bromthymol blue being used as indicator.

The titration result (ml.) multiplied by 56 and divided by 5, gave the barium-soluble value in terms of mgrms. of potassium hydroxide per grm. of fat.

The method, which is simple and rapid, avoids the necessity of eliminating alcohol from the neutral soap solution or of washing the partly-soluble barium soaps with a fixed quantity of water, as in the Avé-Lallement process.

The results show that the barium-insoluble values are somewhat lower than those obtained by the Avé-Lallement method (reduced to the same units), but the difference between the values for normal butters and coconut oil or animal fat is approximately the same. Further, the barium-insoluble values of goats' butter or Syrian samna, in the few determinations made, are no higher than those of gamoos' butter; in fact, a fairly good agreement is revealed in the barium-insoluble values of butters from different sources.

When expressed in the same units (as mgrms. of KOH) the barium-insoluble values of butters, determined by the Avé-Lallement method (Bolton and Revis), lay between about 179 and 187, and the barium-soluble values between 40 and 50, whilst the barium-insoluble values of coconut oil and lard were, respectively, 219 and 189.

As was to be expected, the barium-soluble value increases roughly with the volatile acids of the Reichert–Meissl–Polenske process, and the difference between the two values, expressed in the same units, does not vary widely with butters of the same type. This difference in the accompanying table is seen to vary between the limits of 9 and 16 (as mgrms. of KOH per grm. of fat) for cows' and gamoos' butter, whilst the limits, as determined by the Avé-Lallement process, calculated from the results of Bolton and Revis for cows' butter, lay between 2·6 and 10·1.

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Notes from the Reports of Public Analysts

The Editor would be glad to receive the Annual or other Reports of Public Analysts containing matter of special interest to the Society. Notes made from such Reports would be submitted to the Publication Committee.

COUNTY PALATINE OF LANCASTER

ANNUAL REPORT OF THE COUNTY ANALYST FOR THE YEAR 1933

OF the total number of samples (5635) examined, 5339 were submitted under the Food and Drugs (Adulteration) Act (including 76 appeal-to-cow samples), as compared with 5332 samples in 1932. One hundred and ninety-nine samples were reported to be adulterated.

ARROWROOT.—Between the years 1910 and 1932 inclusive, 1031 samples of arrowroot were examined, and, of these, 15 were found to be adulterated, 11 consisting of maranta starch, with varying quantities of foreign starch, whilst 2 consisted solely of a mixture of maize and potato starches, and 1 of sweet potato starch. The adulteration of arrowroot with sweet potato starch was first recorded by J. R. Stubbs (ANALYST, 1926, 51, 400). More recently Stubbs found small quantities (about 1 to 2 per cent.) of a substance foreign to arrowroot, having some, but not all, of the characteristics of sweet potato starch. The matter was subsequently investigated by P. H. Jones, who found that "marble arrowroot" (*Myrosma cannifolia*) is occasionally mixed with arrowroot by the growers, under the impression that it is a species of maranta (*cf.* Abst., p. 493).

Pearl Barley.—During the years 1926 to 1932 thirteen of the 183 samples examined were faced either with talc (3 samples) or with maize starch (10 samples). The use of maize starch began in the year 1930, increased in amount during 1931, and has since decreased, possibly on account of the attention which has been drawn to the matter. It has been claimed that the use of a coating of talc is necessary to protect the grain from weevils, but Liverseege and Hawley (*J. Soc. Chem. Ind.*, 1915, **34**, 203) were unable to find any evidence of such protective action.

Fat in Cheese.—The following table gives the amounts of fat (calculated on the dry substance) in the samples of cheese examined between the years 1908 and 1932:

Type of cheese	No. of samples	Average Per Cent.	Extremes Per Cent.
American ..	20	52·1	29·2–58·1
Processed ..	17	50·7	45·7–54·9
Cheshire ..	121	50·3	41·1–57·5
Gorgonzola ..	14	49·7	41·0–55·5
Cheddar ..	9	49·6	45·9–53·2
Lancashire ..	98	45·4	42·3–57·1
Soft	12	33·3	2·8–56·1
Dutch	9		29·8–41·0

It is interesting to note that Lancashire cheese contained nearly the same average percentage of fat as Cheshire cheese, although often considered to be richer in fat.

Wine Jelly.—A sample, described on the carton as "Old English Wine Jelly," was found to contain 0·1 per cent. of absolute alcohol, equivalent to about 0·03 per cent. in the jelly prepared for table. The flavour and aroma of the jelly were apparently intended to imitate those of a wine jelly of port character. Wine of port character contains about 15 per cent. of alcohol by volume, so that the alcohol in the sample would correspond with not more than 0·2 per cent. of wine in the jelly prepared for table. The manufacturers have finally agreed to redraft their advertisements.

Lemonade Mixture.—Three samples were returned as adulterated, owing to the absence of citric acid and the presence of tartaric acid.

Rum and Coffee.—A sample labelled "—— the original Rum and Coffee" contained 2·3 per cent. of rum and 30 per cent. of coffee extract, the remainder of the sample consisting of chicory extract and molasses. The sample was an informal one, and further action has not yet been taken.

Labelling of Sausages.—A sample of sausages was found to contain 110 parts of sulphur dioxide per million. When this sample was purchased a notice was exhibited in the shop bearing the following words:—"All sausage sold in this shop contains preservative in accordance with the new Government Regulation." This is a misleading notice, since there is no Regulation which prescribes that sausages must contain preservative; in fact, they may contain preservative only under certain specified conditions.

Where a substance is labelled as containing preservative, the form of label is definitely fixed by the Regulations, and it is further required that:—"No comment on or explanation of the prescribed declaration (other than any direction as to use in the case of a preservative) shall be placed on the label or on the wrapper or container." Apparently no such requirement has been authorised in the case of a notice in a shop and so the misleading form mentioned above cannot, for the moment, be regarded as illegal.

SULPHUR TABLETS.—A sample, submitted as sulphur tablets, was labelled "Lime-juice and sulphur." The tablets were coloured by means of an artificial dye to a pale shade of that yellow-green colour which would appear to be traditionally attributed to lime juice. The tablets were devoid of lime juice, but were flavoured in imitation of essential oil of limes. The vendor has been cautioned.

INDIGO AND TALC IN SWEETS.—An informal sample of boiled sweets was of the praline type, having very dark centres. On examination they were found to contain 0·7 per cent. of some colour having the characteristics of indigo. This is an unusually large amount. Indigo is not one of the prohibited dyestuffs, but the use of such a large amount of any colouring matter does not appear to be desirable.

Another sample of boiled sweets was found to contain about 0·2 per cent. of talc or French chalk. The presence of talc is undesirable, and, as most manufacturers do not use it, apparently unnecessary. Its presence probably arises from the fact that it is used to line the moulds in which the sweets are allowed to set.

G. D. ELSDON

Legal Notes

Under this heading will be published notes on cases in which points of special legal or chemical interest arise. The Editor would be glad to receive particulars of such cases.

INSUFFICIENCY OF WARRANTY

ON May 18th a firm of grocers was summoned at Marylebone Police Court, by the Hampstead Borough Council, for having sold pearl barley which contained 1·2 per cent. of talc and 190 parts per million of sulphur dioxide.

Mr. F. C. Forward, for the Council, said that the barley was bought at a cheap price, and that the presence of talc must have been apparent.

Dr. Cox, Public Analyst for Hampstead, said that the large amount of talc on this barley was very evident, and any grocer could have seen that it was present. He agreed, however, that amounts of talc up to 0·5 per cent. were tolerated on barley and rice, but no sulphur dioxide was allowed in barley.

The defence was a warranty, and evidence was called to prove that those who handled the barley had no reason to believe that it was anything but what the warranty stated. The buyer said that there was nothing about the barley to suggest to him that it was adulterated. It was barley of medium quality costing 8s. 3d. per cwt.

The Magistrate (Mr. Ivan Snell) said that he thought that the buyer had not taken sufficient care, and that the warranty therefore failed. The defendants were fined £2, with three guineas costs.

SALE OF SO-CALLED "DUTCH CHESHIRE" CHEESE AS CHESHIRE CHEESE

On May 10th, 1934, a firm of provision merchants was summoned at Kingston upon Hull Police Court for selling, to the prejudice of the purchaser, 1 lb. of Cheshire cheese which was not of the quality demanded by the said purchaser, inasmuch as it was deficient in fat to the extent of 11 per cent.

Mr. J. E. Fishwick, for the Hull Corporation, said that this was one of those cases in which there was no statutory standard, and that the Stipendiary Magistrate must fix one for himself upon the evidence called before him (*Roberts* v. *Leeming*, 69 J.P., 417; *Wilson and McFee* v. *Wilson*, 68 J.P., 177; *Preston* v. *Jackson*, 1929, S.J., 712). The Corporation contended that the standard for Cheshire cheese was at least 45 per cent. of fat calculated on the water-free substance; evidence would show that the standard of the commercial product was nearer 50 per cent. of fat, but even if his Worship found the standard to be less than 45 per cent., an offence had been committed if he found the standard to be more than 34 per cent. Furthermore, Cheshire cheese was a whole-meat cheese. The sample supplied was found to be deficient in fat to the extent of 11 per cent. (or 25 per cent. calculated on the fat), assuming the standard for fat to be 45 per cent. on the water-free substance.

It was further stated that there was a notice, "Dutch Cheshire" on the cheese. The agent had neither seen nor been able to see the notice until after the purchase. In any case, he would not understand the term "Dutch Cheshire Cheese." A notice, to be a good defence, (*a*) must be either seen by or brought to the notice of the purchaser, and (*b*) the purchaser must understand it. (*Hayes* v. *Rule and Law* (1902), 87 L.T. 133; *Collett* v. *Walker* (1895), 59 J.P. 600; *Star Tea Co.* v. *Neale* (1909), 73 J.P. 511; *Redbourne* v. *Hudson* (1925), 89 J.P. 25).

The Stipendiary Magistrate observed that what the prosecution were really saying was that Cheshire cheese was asked for and that when the sample was analysed it was found to be deficient as Cheshire cheese. Mr. Fishwick agreed.

Evidence was given of the purchase of "1 lb. of Cheshire cheese," for which 8d. was paid. The inspector was subsequently informed that the cheese was not English Cheshire cheese, but was "Dutch Cheshire" cheese. On leaving the shop the witness noticed on the display counter a label marked "Dutch Cheshire." He had not noticed it previously, and could not have seen it from where he was served.

Mr. A. R. Tankard, F.I.C., the Hull City Analyst, said that the sample was not Cheshire cheese. Cheshire cheese was a whole-meat cheese, *i.e.* one made from substantially whole milk. The sample contained 16·3 per cent. of fat, whilst Cheshire cheese would have contained 24 per cent. or more of fat. Calculated on the dry substance, the fat in the cheese was 34 per cent., whilst in a whole-meat cheese the minimum should be 45 per cent. on the dry substance. He had never met with Cheshire cheese containing less than 45 per cent. of fat.

Of 132 cheese samples passing through his hands, 49 were sold as Cheshire cheese, 35 being purchased prior to this year, the minimum fat-content being 47 per cent. on the dry matter. The maximum was 60 and the average 52. Of the 12 samples bought this year since the sample at issue, the fat average was 51·2 per cent. on the dry matter; the lowest figure was 46·8, and the highest 57·6, so that the average amount of fat in Cheshire cheese, as now sold in Hull, was 51·2 per cent. It not only complied with the standard set up (45 per cent. fat on the dry matter), but more than complied with it. The sample in question was a skimmed-milk cheese. Cheshire cheese was known to him as a whole-meat cheese, because (i) of the method of manufacture; (ii) his experience as a Public Analyst confirmed that it was a whole-meat cheese; (iii) the published authorities so described it; and (iv) the Government had accepted this standard of 45 per cent. fat as a general requirement in connection with the grading of Cheshire cheese.

The witness quoted authoritative publications showing that Cheshire cheese was made from substantially whole milk, and he stated that as a whole-meat cheese it contained a ratio of fat to protein which was characteristic. The fat usually exceeded the protein in amount, and the ratio of fat to protein varied from 1·0 to 1·5 : 1. On the other hand, the amount of protein exceeded the fat in skimmed-milk cheese, and this ratio was then less than 1·0 : 1. The present sample had a fat : protein ratio of 0·63 : 1.

Mr. Tankard went on to show that 1000 lbs. of milk (97 gallons) would yield from 94 to 100 lbs. of cheese, according to fat-content and other factors. He calculated that milk containing the minimum of 3·0 per cent. fat would yield a cheese containing at least 46 to 51 per cent. of fat according to the probable amount of moisture present, and 52 to 58 per cent. of fat if the yield of cheese was less than 10 per cent. of the weight of milk used. In further proof of his statement that this cheese was a skimmed-milk cheese, and therefore not a Cheshire cheese, he calculated, by a well-known formula, that from its composition it was made from milk containing not more than 2·0 per cent. of fat. The deficiency in fat of this cheese meant a loss in energy-value as compared with a whole-meat cheese, which had 100 points of food value (expressed as calories) compared with 66 points for the skimmed-milk cheese sold to the sampling officer. The witness expressed his firm opinion that this sample of cheese could not be described as "Cheshire cheese"—it was not Cheshire cheese.

In cross-examination the witness agreed that the Ministry of Agriculture had not fixed a standard for fat in cheese. He did not agree with the suggestions made by Mr. Pearlman that the real reason why no fat-standard had been fixed was that there was a demand for cheap cheese of Dutch type which the country was not producing adequately, or that in Cheshire, in order to meet this demand, there was a great variation in the percentage of fat in Cheshire cheese.

Mr. S. Ernest Melling, F.I.C., Public Analyst for the County of Cheshire, etc., said that he had analysed a portion of the sample of cheese in this case, and found 16·2 per cent. of fat. He agreed substantially with Mr. Tankard's opinion on this sample as expressed in his certificate. On the 45 per cent. fat-standard, the fat was deficient to the extent of 22 per cent. Mr. Melling said that his analyses of nearly 1000 samples of cheese submitted as "Cheshire cheese" showed it to be a whole-meat cheese containing from 46·4 to 61·4 per cent. of fat on the dry solids. He had not come across a Cheshire cheese deficient in fat for several years. He had made investigations into the composition of Cheshire cheese produced strictly by the usual methods, and had found that, following the process throughout, a milk containing 3·44 per cent. of fat and 8·80 per cent. of non-fatty solids yielded about 10 per cent. by weight of cheese containing 36·0 per cent. of moisture, 33·65 per cent. of fat, and, on the dry matter, 52·6 per cent. of fat. Similarly, when the milk used contained 2·71 per cent. fat, the cheese showed 43·7 per cent. of water, with 24·9 per cent. of fat or 44·1 per cent. of fat on the dry matter. It would appear quite certain that the sample of cheese in question here was derived from milk containing about 2 per cent. of fat. Such a cheese was not entitled to be called "Cheshire cheese," which, in food-value, was 50 per cent. superior. He did not recognise, he said in cross-examination, "Dutch Cheshire cheese," which was a misnomer.

Mr. W. B. Mercer, B.Sc.(Agric.), Principal of the Cheshire School of Agriculture, also gave evidence. Cheshire cheese, he said, was universally regarded in his area as a whole-meat cheese, and he accepted the definition of whole-meat cheese which had been given. The method of manufacture of this cheese involved the use of whole milk, and the product invariably contained over 45 per cent. of fat on the dry matter. The average fat in Cheshire cheese was found by him in

1928 to be 49 per cent. on the dry sample, and similar figures could be quoted for later years (an average of 51·9 per cent. of fat on 68 recent samples). The Cheshire Cheese Federation had adopted the standard of 45 per cent. on the dry matter of the cheese as a guaranteed minimum.

Mr. Pearlman, for the defence, emphasised the point that the notice was conspicuously displayed on the cheese, and it should have prompted the purchaser to inquire what he was getting. He did not demand any quality, but asked for Cheshire cheese and received Dutch Cheshire cheese.

The Stipendiary Magistrate, announcing his decision, said that he thought it should be made absolutely clear that this was not a case of passing off foreign produce as British produce and describing it as such. When people went into a shop, he continued, they were entitled to get what they asked for, or to be told that the shop did not sell it. He found that the purchaser in this case did not see the notice referred to. With regard to Mr. Pearlman's second point, that Dutch Cheshire cheese was Cheshire cheese, the Stipendiary Magistrate accepted the evidence of the Corporation's witnesses as to what had to be found in Cheshire cheese before it could be so called. He had no difficulty in saying that the cheese concerned in this case was not Cheshire cheese, and was therefore not the cheese for which the Corporation's representative had asked. Imposing the maximum penalty with £15 15s. costs, Mr. Macdonald said that he thought people of the standing of the defendants—who were not small shopkeepers—were people who could have afforded to take expert advice on such a point before starting to sell the article under any description.

Department of Scientific and Industrial Research

THE INDUSTRIAL APPLICATION OF X-RAY CRYSTAL ANALYSIS*

In this pamphlet of 15 pages an explanation is given, with photographic illustrations, of the ways in which X-rays are now used to determine the structure and condition of materials used in industry.

The Introduction describes briefly the principles of the method, and shows how the nature of the pattern produced by the diffracted rays, and recorded on a photographic plate, depends not only on the chemical structure of the material, but also on other factors, such as the size of the crystal grains, the distribution in direction of these grains, and the approximation to perfection attained by the crystals during their growth.

The information to be derived from the X-ray pattern is summarised under the following heads:

The General Nature of the Material.—Single crystals and crystal aggregates give different types of pattern, the former consisting of isolated spots, and the latter of a series of continuous lines. Problems concerned with single crystals seldom arise in practice; one example is the determination of the orientation of synthetic jewels used as pivot bearings. The wear and friction depend on the nature of the crystal plane on which the pivot rotates, and this plane can readily be determined by an X-ray examination.

The Size of the Crystal Grains.—The nature of the pattern varies with the grain size, and has one of three forms according to the size. When the linear size is much less than 10^{-5} cm. the lines lose their sharpness, and the size of the crystals can be measured by measuring the increase in the breadth of the lines. Measurement of crystal grain size is of great importance in such questions as the spreading power of paints, the activity of catalysts, and the physical properties of electro-deposited metals and metals in general.

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* London: Issued by the Department of Scientific and Industrial Research, 16, Old Queen Street, Westminster, S.W., May 28th, 1934. Enquiries concerning the facilities of the National Physical Laboratory for carrying out investigations on X-ray crystal analysis should be addressed to the Director, the National Physical Laboratory, Teddington, Middlesex.

THE ORIENTATION OF THE CRYSTALS IN AN AGGREGATE.—The crystals of an aggregate may be distributed entirely at random, or may show a more or less pronounced tendency to take up some particular orientation. This occurs frequently as a result of cold-work processes, such as the rolling and drawing of metals, and is also characteristic of many fibrous substances. Successful applications of the method have been made in the study of metals (in which the presence of fibre structure is of great importance), textile fibres, rubber, etc.

THE STATE OF PERFECTION OF THE CRYSTALS.—The presence of internal strain results in a distortion of the crystal cells, and this distortion shows itself in the X-ray pattern by a loss of sharpness of the diffraction lines. If the breadth of the lines is measured, a measure of the degree of strain is obtained. The method is not confined to the study of metals or the detection of strains in castings, welds and the like, but is also applicable to other substances such as natural graphite, the physical properties of which vary with the degree of imperfection of the graphite crystals formed from the amorphous carbon.

THE CHEMICAL NATURE OF THE MATERIAL.—Each chemical compound (not merely each chemical element) has its characteristic atomic arrangement, and its own characteristic X-ray diffraction pattern by which it can be identified. An approximate analysis is usually practicable, although exact quantitative analysis by means of X-rays presents considerable difficulties. Moreover, the method fails to take account of amorphous material. An example of the application of X-rays to chemical problems is afforded by the determination of the composition of thin scales on steel boiler tubes which had burst under puzzling conditions. Without removing the scale, the particular oxides of iron forming it were identified not only at different points on its surface, but also at different depths.

Other chemical applications consist in the detection of impurities, the study of solid solutions and mixtures, and the examination of allotropic modifications. For example, by the use of X-rays it is possible to determine immediately whether a specimen of silicon dioxide is α- or β-quartz, cristobalite or tridymite.

CHANGES IN STRUCTURE PRODUCED BY PHYSICAL TREATMENT.—A typical example of this application of the method is its use in the examination of magnet steel before and after heat-treatment in manufacture. It is shown how an internal strain, which is apparently desirable in such steel, disappears if the steel is heat-treated at 900° C., but reappears when it is heat-treated at 1200° C. On the other hand, experiments on two electrical transformer steels show how the magnetic losses of such steels are reduced as the crystals are rendered free from strain, as indicated by the X-ray photographs.

Ministry of Health

ANTIMONY IN ENAMELLED HOLLOW-WARE*

In a special report (No. 29) issued by the Ministry in 1925 (*cf.* ANALYST, 1925, **50**, 133) on the solubility of glazes and enamels used in cooking utensils, attention was drawn to the possible toxic effect of antimony oxide. Since this report was published several outbreaks of poisoning, affecting large numbers of people, have occurred (*cf.* Dunn, ANALYST, 1928, **53**, 532), and, in view of the possibility that further and still more serious outbreaks might occur, the Ministry issued a warning (Ministry of Health Memo. 171/Med. 1933; ANALYST, 1933, **58**, 226) that enamelled hollow-ware vessels obviously intended for other purposes may be dangerous if used for the preparation or storage of food or drink. Further enquiries have shown that antimony enamels are used also for cooking vessels, and although no cases of illness definitely diagnosed as antimony poisoning have been traced to the use of enamelled cooking vessels, there is the possibility of chronic impairment of health from the continued ingestion of small doses of antimony.

THE ENAMELLING OF HOLLOW-WARE.—The vessel is spun or pressed from sheet iron and coated with a frit composed of some or all of the following ingredients: Borax, felspar, quartz, fluorspar, cryolite, lime, magnesia, sodium nitrate, which are mixed with water and china clay, and an opacifying agent. It is then dried and the coating is fused on to the metal in the enamelling furnace. Tin oxide is widely used to render the enamel opaque, but owing to its high price has been largely replaced by antimony, in the form either of trioxide or of sodium metantimonate. The former is used in this country and on the Continent, a well-known brand being "Timonox," whilst the latter is used to a limited extent on the Continent under the name "Leukonin" (*cf.* Beck and Schmidt, *Z. Unters. Lebensm.*, 1928, **55**, 1; Abst., ANALYST, 1928, **53**, 302). Oxides of cobalt, iron, manganese, nickel, etc., are also introduced into the enamel according to the colour required. Antimony trioxide is almost invariably fritted with the enamel mixture, whereas sodium metantimonate is usually added in the mill. These facts have an important bearing upon the state of oxidation of the antimony in the finished enamel.

The amount of silica in the enamel is of primary importance in connection with the contamination of food by antimony. A low silica-content, with corresponding preponderance of bases or boric acid, renders an enamel easily corroded, whilst a "hard" enamel, with high silica-content is less readily attacked. Since, however, "hard" enamel is more difficult to frit, and requires a higher temperature in the enamelling furnace, it is more expensive to produce, and the tendency is to use "soft" enamels on ware not intended for cooking purposes.

STABILITY AND SOLUBILITY OF ANTIMONY OXIDES.—Antimony pentoxide, when heated at temperatures above 440° C., loses some of its oxygen and forms lower oxides. The tetroxide is stable at all temperatures up to that of the gas blowpipe. The trioxide melts at a red heat and, on further heating, partly volatilises. Sodium metantimonate, $Na_2O.Sb_2O_5.7H_2O$, becomes anhydrous at 350° C., and does not lose oxygen until temperatures above 1000° C. are reached. Commercial anhydrous metantimonate contains about 11 per cent. of sodium, but preparations with much less sodium than this (apparently mixtures of antimony pentoxide and sodium metantimonate) are sold for use in certain kinds of enamel.

Antimony trioxide and pentoxide and sodium metantimonate are all more or less soluble in tartaric acid solutions. A fairly accurate separation of the trioxide from the other two oxides may be effected by treatment of the mixture at room temperature with 2 N hydrochloric acid, in which the pentoxide is only slightly soluble.

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* By G. W. Monier-Williams, O.B.E., Ph.D., F.I.C. Reports on Public Health and Medical Subjects. No. 73, pp. 18. H.M. Stationery Office, 1934. Price 4d. net.

THE TOXICITY OF ANTIMONY COMPOUNDS.—Some of the recorded observations appear to be rather contradictory, but it seems clear that only soluble compounds of tervalent antimony are definitely and actively toxic. Soluble compounds of quinquevalent antimony are relatively harmless, although probably not absolutely non-toxic. Insoluble compounds of antimony in either state of valency appear to be relatively harmless.

THE ACTION OF TARTARIC ACID SOLUTIONS ON ENAMELLED HOLLOW-WARE.—In the experiments described, samples of wrought hollow-ware, obtained in the course of visits to various factories, were tested with boiling 2 per cent. tartaric acid solution, 500 ml. of which were poured into the vessel and left for an hour, with occasional stirring. The solution was then poured off and diluted with water to 500 ml., and aliquot portions were used for the determination of total antimony and tervalent antimony. Details of the procedure are given.

STATE OF OXIDATION OF ANTIMONY IN ENAMELS.—The method of determination of the trioxide and pentoxide is described in detail, and a table is given of the results obtained with 11 samples of hollow-ware. The figures indicate that when antimony trioxide is used in the enamelling process 50 per cent. or more becomes oxidised to higher oxides, owing probably to the presence of nitrates in the frit-mixture, and to absorption of oxygen from the air. When used as sodium metantimonate in the mill the antimony is partly reduced to trioxide, but the greater part remains in the quinquevalent state. In general, both oxidation and reduction of antimony compounds may occur in the fritting furnace. Antimony compounds added in the mill remain, for the most part, unaltered.

GENERAL CONSIDERATIONS.—Although the use of antimony in hollow-ware might be brought under control by (*a*) marking or labelling enamelled goods containing antimony, (*b*) applying a solubility test, or (*c*) allowing only the pentoxide or its compounds to be used, it is doubtful whether these measures would be entirely effective, and it is suggested that total prohibition of antimony in hollow-ware might be found to be in the best interest both of the public and of the trade.

Straits Settlements

ANNUAL REPORT OF THE GOVERNMENT ANALYST FOR THE YEAR 1933

THE greater portion of the routine work of the Government Analyst's Department is provided by the Monopolies Department, and is concerned with the protection of revenue. It consists in the examination of opium, chandu, chandu dross, imported or locally distilled liquor, toddy and deleterious drugs. Work is also done for other Government departments, including the examination of exhibits from the Police Department. The Government Analyst (Mr. J. C. Cowap) gives details of all work undertaken in the main laboratory at Singapore and in the Penang branch laboratory. The total number of samples examined in the former laboratory was 14,345, and in the latter 3550.

COMPOSITION OF SINGAPORE MILK.—With the assistance of the Chief Health Officer, 129 samples of fresh cows' milk were taken for analysis under conditions which ensured the integrity of the milk and the completeness of the milking, the object being to attain a knowledge of what the quality of fresh milk sold in Singapore ought to be. The samples were taken from the mixed milk of small herds of cows (numbering from two to twelve), such as are kept by the usual milk-seller. The average figures were:—Sp.gr. at 15·5° C., 1031·5; fat, 5·13 per cent.; solids-not-fat, 9·42 per cent. The highest figure for fat was 9·3 per cent. (from the mixed milk of two cows) and the lowest 1·4 per cent.—also from the mixed milk of two cows.

Six samples of buffalo milk, similarly taken, gave as average figures:—Sp.gr., 1029; fat, 8·5 per cent.; solids-not-fat, 9·8 per cent.

DELETERIOUS DRUGS.—Seventy-six exhibits were examined in cases of possession or importation of deleterious drugs. Most of these contained Indian hemp, but a number of medicines were found to contain morphine, and one large seizure consisted of a number of tins containing pure cocaine hydrochloride and other tins containing a mixture of cocaine hydrochloride with a synthetic cocaine substitute. This method of adulterating cocaine has not been previously met with in the Colony.

COUNTERFEIT COINS.—Exhibits were received in 14 cases connected with counterfeit coins. In some of these cases complete outfits were found for making coins from fusible alloys. The usual alloy is made from tin, lead and antimony, but one lot of coins was made from an alloy of zinc with copper and aluminium, and another lot appeared to have been made from chandu tubes.

Twenty-six Straits Settlements 10 cents pieces and five Netherlands India half-guilders were found to be made from a silver-copper alloy and were counterfeit.

In one case a large number of coins appeared to have been defaced on one side and to have been re-engraved. As they were of the correct fineness of genuine coins, it was presumed that they had been used as buttons and afterwards re-converted to their original purpose.

EVIDENCE FROM DEPOSIT ON FEET.—In an interesting case a man accused of possession of goods which had been stolen from a house was found to have adhering to the inside of each foot a heavy blackish deposit. He was brought for examination and the substance scraped from the feet when examined microscopically was seen to consist of masses of two kinds of blue-green moulds, which were identified with moulds growing on the wall of the house from which the property had been stolen. Photomicrographs of the two were identical, and the man was convicted of house-breaking.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs Analysis

Contents of Phosphorus, Sulphur, and Alkalis in Hens' Eggs. J. Grossfeld and G. Walter. (*Z. Unters. Lebensm.*, 1934, 67, 510–529.)—In agreement with published data, the yolk of the hen's egg contains, on the average, 1·42 per cent. of P_2O_5 or 2·78 per cent. on the dry matter, whereas the white contains 0·036 per cent. (0·28 on dry matter). The P_2O_5 of the lecithin amounts to 1·01 per cent. of the natural, or 1·98 per cent. of the dried yolk. One part of total P_2O_5 corresponds with 70 parts of yolk or 36 parts of dry yolk, and with 189 (50) parts of natural (dry) egg-contents. Similarly, 1 part of lecithin-P_2O_5 corresponds with 99 (50) parts of natural (dry) yolk or with 277 (73) parts of natural (dry) egg-contents. The ratio of total to lecithin-P_2O_5 is 1·41 for the yolk and 1·47 for the total egg-contents. In determining the total phosphoric acid, and in the conversion of the extracted lecithin into phosphate, good results are obtained by incineration in presence of magnesium acetate. For extracting the lecithin, practically equal yields are obtained by using either alcohol, a mixture of 4 parts of benzene with 1 part of alcohol, *iso*propyl alcohol, propyl alcohol, or methyl alcohol.

Calculation of the sulphur-contents of yolk and white from those of the various proteins present gives results agreeing with those of actual determinations. For egg-white the mean percentage of sulphur is 0·212 (1·67 on dry matter), and for yolk 0·222 (0·436 on dry matter). By simple incineration, even in presence of alkali, considerable loss of sulphur is incurred, and many incorrect published data have resulted therefrom. Good results are obtained after preliminary fusion with potassium hydroxide and nitrate in a silver crucible.

The average percentages of potassium and sodium are 0·112 and 0·045 respectively in the fresh yolks, and 0·153 and 0·179 respectively in the white. For determining potassium, the perchloric acid method, following fusion with barium acetate and treatment of the solution of the fused mass with baryta, proves satisfactory. The sodium may be determined, either indirectly in the same solution, or by incinerating a fresh quantity of material with magnesium acetate and applying Barber and Kolthoff's method (ANALYST, 1928, **53**, 456).

T. H. P.

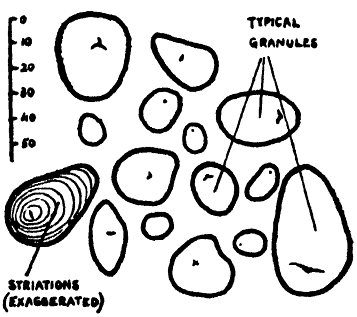
Colorimetric Determination of Manganese in Flours and Breads. P. Bruère. (*Ann. Falsificat.*, 1934, **27**, 150–157.)—The colorimetric determination of manganese furnishes information additional to that given by the ash determination in flours, and more particularly for breads suspected of addition of inferior products. It has been found that, calculated on 100 grms. of the dry material, 0·7 mgrm. of manganese is present, on the average in the wheat grain albumen, 13 mgrms. in the envelope and 19 mgrms. in the germ, giving a mean total of 2·881 mgrms. for the whole grain of average weight (weight of 1000 grains about 50 grms.). In the albumen (*i.e.* the central part of the grain) only about 0·4 mgrm. per 100 grms. is present, whereas the periphery has about 3 times as much; the external zone of the envelope (about 38 per cent.) contains much less manganese than the internal zone. To determine the proportion of manganese present, the white ash from 10 grms. of flour or 5 grms. of offal, is taken up with 10 ml. dilute (1:4) nitric acid, the mixture is filtered through an asbestos plate into a pyrex tube, the boiled water used for washing being added to the filtrate, and 5 drops of 0·1 *N* silver nitrate solution are added as catalyst, followed by 1 to 2 dgrms. of finely powdered potassium persulphate. The mixture is gradually heated to boiling, and as soon as the gas has been driven off, 20 ml. of water are added. The colorimetric determination is made at once either by comparison in a colorimeter with a solution of potassium permanganate of known strength, or with the aid of a colour-scale prepared from a solution of manganese sulphate (4·054 grms. to 4 mols. of water per litre), diluted when required. D. G. H.

Detection of Flour from Denatured Wheats. Identification of the Colouring Matter. J. Meyer. (*Ann. Falsificat.*, 1934, **27**, 174–175.)—In order to detect wheat flour which has been denatured with the aid of methylene blue or eosin, 25 to 30 grms. of the flour are spread out in an even layer, 3 mm.

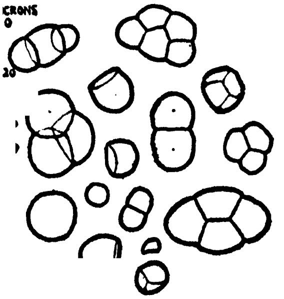
thick, on a glass plate, compressed by means of a white paper to a layer about 1 mm. in thickness, and moistened with 25 ml. of a mixture of 70 parts of 95 per cent. alcohol, 10 parts of glycerin and 20 parts of water, applied to the centre of the flour by means of a pipette with a fine jet. After 15 minutes' contact the slightest trace of colouring matter becomes apparent as a fresh stain of blue or pink, and such stains are best seen by examining the layer of flour by transmitted light. Occasionally the accidental presence of the débris of coloured vegetable fibres will give rise to different coloured stains. Examination under the microscope may then be necessary. By comparison with a type sample of flour similarly treated, the addition of lower grade flour to high grade flour may be detected.

D. G. H.

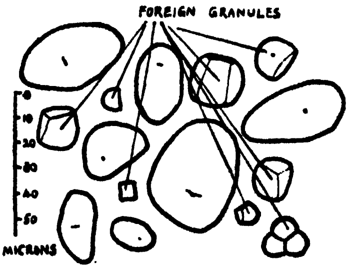
"Marble" Arrowroot. P. H. Jones. (*Food*, 1934, 3, 225–228.)—Arrowroot has been defined by the Government of St. Vincent as "the separated and purified starch from the rhizomes of the plant known as *Maranta arundinacea*," and this is the definition ordinarily accepted in the trade. During the war extensive adulteration of arrowroot with sweet potato starch was undoubtedly practised, but of late years there have been reports of the presence in arrowroot of small and varying quantities of a starch similar to sweet potato starch. The difficulties of accounting for the presence of sweet potato starch led to a search for a possible adulterant starch having similar truncated granules. It was found that a bulb-shaped tuber known as "marble" arrowroot grew in some plantations, and since it was thought by the planters to be an arrowroot, it was pulped with the true arrowroot, and thus gave rise to the small varying amounts of "sweet potato" reported. The granules of this starch are truncated, but rather smaller than those of true arrowroot (10–30μ).[*] The "marble" arrowroot bulb has been identified at Kew as *Myrosma cannifolia* (synonym *Calathea myrosma*, Lindley), and Professor Cheeseman of Trinidad reported it as belonging to the *Marantaceae*, but not of the genus *Maranta*, and therefore not an arrowroot. The plant grows wild in St. Vincent, Guiana and Brazil. Steps are now being taken to have this "marble" arrowroot eradicated, so that, in future, it shall not render imports liable to be condemned under the Food and Drugs Act. (*Cf.* p. 482.) D. G. H.



Maranta Starch



"Marble" Arrowroot Starch



Maranta Starch containing "Marble" Arrowroot Starch

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[*] These diagrams were drawn for THE ANALYST by Mr. A. H. Leather.—EDITOR.

Composition of the Glycerides of Coffee-Bean Oil. R. O. Bengis and R. J. Anderson. (*J. Biol. Chem.*, 1934, **105**, 139–151.)—The authors (*J. Biol. Chem.*, 1932, 97, 99; Abst., ANALYST, 1932, 57, 579) have shown that the unsaponifiable matter of the coffee-bean oil consists largely of a crystalline substance named kahweol, and that ordinary phytosterol is present only in small amounts in this fraction. A report is now given which deals with the composition of the oils obtained by extraction from the natural raw bean, the freshly roasted, and the stale roasted coffee-bean, and with the component fatty acids of the glycerides. Previous work by various authors is briefly discussed. The results show that there is no appreciable loss or change in the amount of fat of coffee-beans on roasting or ageing. The fragrant odour and flavour of the fat from freshly-roasted coffee disappear on ageing, and are replaced by an unpleasant rancid odour. A distinct increase in the water-soluble volatile acids occurs in the fat from the stale roasted beans. The unsaturated fatty acids, representing about 52 to 54 per cent. of the total acids, are composed approximately of equal parts of oleic and linolic acids. The solid saturated fatty acids consist mainly of palmitic acid, but small amounts of stearic acid and a tetracosanic acid are also present. An unsaturated, optically active, hydroxy acid of high molecular weight was present in the liquid acid fraction of all of the three fats examined. The oil contains a very small amount, (about 0·1 per cent) of phosphatid, which can be precipitated by acetone. The following results were obtained in the analyses of oils extracted from the beans with petroleum spirit:

	Fat extracted Per Cent.	Iodine value (Hanus)	Sapon. value	Reichert-Wollny value	Unsap. matter Per Cent.	Total fatty acids Per Cent.	Liquid acids Per Cent.	Solid acids Per Cent.	Acetone-insol. phosphatid Per Cent.
Green beans	81·1	97·8	179·3	0·56	9·0	86·5	52·3	39·4	0·1
Freshly roasted	90·4	96·0	172·1	0·86	10·2	87·0	54·4	37·5	0·08
Stale roasted	86·3	95·6	171·9	1·97	9·65	86·7	54·5	37·4	0·21

P. H. P.

Determination of Starch in Paprika adulterated with Flour. D. Kőszegi and N. Tomori. (*Z. Unters. Lebensm.*, 1934, **67**, 538–541.)—The finely-ground paprika is passed through a fine cloth sieve, and 5 grms. are dried for 1 hour at 100° C., and then extracted with ether for 3 hours in a Soxhlet apparatus. The oil-free residue is transferred to a 100-ml. centrifuge tube, in which it is well mixed with water at 35° C., and centrifuged at 4000 revolutions per minute. After removal of the clear aqueous solution, this operation is repeated six times. The final residue is thoroughly ground in a porcelain mortar with 10 ml. of water, 40 ml. of concentrated hydrochloric acid (sp.gr. 1·19) being added gradually during the grinding. After 30 minutes, the contents of the mortar are transferred, with the help of 25 per cent. hydrochloric acid, to a 200-ml. measuring flask, and made up to volume with 10 ml. of 4 per cent. sodium phosphotungstate solution and 25 per cent. hydrochloric acid. After filtration, the clear liquid is polarised (as soon as possible) in a 2-dm. tube. The number of grms. of starch per 100 ml. of solution is given by $100\alpha \div 202l$, where α is the observed angular rotation and l the length of the observation tube in dm. [*i.e.* (2)]. Multiplication of the resulting number by 40 gives the percentage of starch in the paprika. This percentage must be diminished by 1·1, since, when treated as above, pure paprika gives a solution with a rotation of 0·1 to 0·12°, corresponding with 1·1 per cent. of starch. Test determinations on mixtures of paprika with maize-, wheat-, and rye-meals in various proportions gave satisfactory results. T. H. P.

Effect of Wrapping Material on the Fat of Fatty Foods. I. Contact Wrappers, Vegetable Parchment, Greaseproof Paper. II. The Effect of Sunlight passing through Transparent Wrappers of Various Colours (Cellophane) and Some Transparent Papers. W. L. Davies. (*J. Soc. Chem. Ind.*, 1934, **53**, 117–120T; 148–150T.)—I. The investigation of the copper- and iron-contents of vegetable parchment from various sources; of greaseproof paper, and of the wood cellulose pulp used for the manufacture of vegetable parchment (37 samples in all), showed that hard neutral vegetable parchment from British and Continental sources, and also wood cellulose pulp, contained on an average 22 p.p.m. of copper and 50 p.p.m. of iron. Practically no copper or iron was added during manufacture, except in the case of loaded samples, and on an average one-seventh of the iron and one-tenth of the copper of the hard neutral products were water-soluble. At p_H 5·6 about half the copper and one-seventh of the iron of British parchments were soluble in acetate buffer, but about 44 per cent. of the iron of Continental samples; at p_H 4·6, 42 to 87 per cent. of copper and 30 to 58 per cent. of iron were soluble. On the whole, the solubilities for soft parchments and for greaseproof paper were higher. In experiments designed to intensify the conditions necessary to cause fat autoxidation, it was found that peroxide formation was greatest with cotton wool, but with glass wool, vegetable parchment and sulphite pulp the rates were very similar. It appears that, in spite of the high content of iron and copper of hard neutral parchment, the effect of the metals is not appreciable within the range of acidities found in fatty foods during the usual storage time.

II. Eleven samples of variously-coloured cellophane were examined by actinometric reagents and by studying the rate of autoxidation of butter-fat and of the fat of biscuit meal wrapped in the samples. The samples divided themselves into 3 classes: (i) with no appreciable absorption of the chemically active rays, autoxidation consequently occurring practically as with direct exposure (colourless, light blue, pink, orange and lemon cellophanes); (ii) samples showing considerable absorption, and some autoxidation of the wrapped fat, but with evidence of a slow actinic effect (heliotrope and light green); and (iii) samples with complete, or nearly complete, absorption, and consequently with no appreciable increase of the peroxide oxygen of the wrapped fat (deeply coloured samples, green, blue, brown and red). Vegetable parchment allowed very little actinic light to pass; greaseproof paper fell into class (ii), and transparent papers were almost completely transparent to the active rays. Wax paper was opaque to active rays, but, in contact with dry fatty foods, volatile products of autoxidation of the wax appeared to initiate autoxidation of the fat of the wrapped food. The cellophanes showed a connection between the rate of autoxidation of the wrapped fatty material and the intensity of colour, irrespective of the colour of the sample. Absorption of the chemically active rays was thus co-relative with depth of colour and extinction coefficient, with the absorption in the region 400–500$n\mu$ by one thickness, and with the rate of increase of extinction by increasing the number of thicknesses of the cellophane. D. G. H.

Colorimetric Determination of Cantharidin. G. Denigès. (*Compt. rend.*, 1934, **198**, 1783–1785.)—When heated and shaken with formaldehyde and concentrated sulphuric acid, cantharidin gives a brown to black colour, and the reaction will detect 0·01 mgrm. of cantharidin. For comparative tests a series of standards is prepared by using increasing quantities of an acetic acid solution of cantharidin of such a strength that 1 drop corresponds with, say, 0·05 mgrm. of cantharidin, and adding to each the same volume of sulphuric acid. The sample should be diluted, if necessary, but the colorimeter comparison should then be made quickly, as the brown substance, which is in an unstable colloidal state, coagulates after a time. Other substances may give a brown colour in the presence of sulphuric acid, but cantharidin does so only in the presence of formaldehyde. The method may be used directly on chloroform decoctions of vesicant insects. After identification of the micro-crystals the quantitative determination may be made on an aliquot part of the solution. D. G. H.

Biochemical

Composition of Sweat. B. A. McSwiney. (*Lancet*, 1934, **226**, 641.)—Water is lost from the skin in two ways—by evaporation from the epithelial surface and by secretion through the sweat glands. The sweat may be strongly hypotonic in comparison with blood plasma, yet may remove what may be large amounts of sodium chloride from the body. Under normal conditions 600 to 700 ml. of sweat are evaporated from the skin in 24 hours. The constituents of sweat are very variable. The following table gives the average values calculated from the examination of 14 male and 10 female specimens:

		Mgrms. per 100 ml.				
Subject	p_H	Ammoniacal nitrogen	Urea	Amino-acid nitrogen	Glucose	Chlorides (NaCl) Grms. per 1000 ml.
Female	6·57	6·0	19·23	6·5	20·0	3·00
Male	6·14	4·7	21·44	5·0	12·6	3·70

Traces of creatine and creatinine have been found, and lactic acid is present in amounts not greater than 120 mgrms. per 100 ml. Examination of the sweat shed by rheumatic subjects shows no marked divergence from the normal. The secretion of sweat is under control of the nervous system, the sweat glands being innervated by sympathetic fibres, and the nervous mechanism may be called into action by central stimuli, by reflex action, or by peripheral stimuli. Adrenaline has no action on the glands, whilst pilocarpine excites and atropine paralyses them. Recent work suggests that the impulses are chemically transmitted by acetylcholine, liberated at the nerve-endings and acting on the sweat glands. P. H. P.

Influence of Fluorine Ingestion upon the Nutritional Qualities of Milk. P. H. Phillips, E. B. Hart and G. Bohstedt. (*J. Biol. Chem.*, 1934, **105**, 123–134.)—Nutritional studies on the inclusion of small but constant amounts of fluorine in the dietaries of different species of animals have shown that the practice is fraught with considerable danger. Since fluorine-bearing mineral supplements are in use for feeding dairy cattle, milk might thus have a sufficiently increased fluorine-content to produce harmful effects. Studies were made to determine whether the nutritional qualities of milk were influenced by different levels of fluorine intake, such as might be encountered in ordinary dairy cattle-feeding. The problem was approached in two ways: (i) by a biological test of the milk from controls and from rock phosphate-fed Holstein cows, and (ii) by a systematic study of the fluorine-content of the milk produced by these cows. The results show that mineralised milk samples from individual cows may cause variable milk consumption in rat-feeding experiments; the cause of such variation is not clear. No difference was observed in the biological reaction of rats given normal milk, as compared with those fed with milk from cows receiving an added source of fluorine. Fluorine determinations of milk from cows receiving no added fluorine in their normal ration and from those receiving added sources of fluorine showed that they were not widely different with respect to their fluorine-content. The range of fluorine in normal milk was found to be 0·05 to 0·25 mgrm. of fluorine per litre, with an average value of 0·138 mgrm. The lactation (first, second or third) or period of lactation was without effect on the fluorine-content of the milk. Fluorine added to milk diets resulted in a higher residual fluorine in the body ash. The storage of fluorine was not proportional to the total fluorine intake. Apparently, a mechanism of elimination operates beyond certain threshold limits. No noticeable difference was demonstrated between the residual fluorine of the body ash of rats fed with milk from cows receiving no added source of fluorine and those fed with milk from cows receiving an added source of fluorine. Diets with traces of fluorine ranging from 4·5 to 132·0 micro-grms. of fluorine per rat per day produced no detectable toxicosis; these levels of fluorine intake are without effect, and it seems likely that no stimulation of physiological processes can be attributed to small non-toxic doses of fluorine. The fluorine-content of milk is comparatively difficult to influence by dietary means. This does not preclude the possibility that the use of a more soluble form of fluoride in equal or larger doses might increase the fluorine-content of milk. It is apparent that fluorine in concentrations greater than 1 part in 10 in the diet has no essential function in the metabolism of the rat.

P. H. P.

Influence of Breed and Diet of Cows on the Carotene and Vitamin *A* Content of Butter. C. A. Baumann, H. Steenbock, W. M. Beeson, and I. W. Rupel. (*J. Biol. Chem.*, 1934, **105**, 167–176.)—Spectroscopic determinations have been made of the carotene and vitamin *A* content of butter-fat from cows of various breeds on high and low carotene diets. Definite breed differences were noted. On the winter ration, average carotene values ranged from 4·3 micrograms per grm. for Holstein butter to 7·8 micrograms per grm. for Guernsey butter; vitamin *A* ranged from 5·1 micrograms per grm. for Guernsey butter to 10·1 micrograms per grm. for Holstein butter. On the green feed ration, averages for carotene ranged from 5·5 micrograms per grm. for Ayrshire butter to 17·0 micrograms per grm. for Guernsey butter; vitamin *A* ranged from 8·5 micrograms per grm. for Guernsey butter to 15·1 micrograms per grm. for Holstein butter. When butters from different breeds on the same diet were compared, inverse relations between the carotene and vitamin *A* were revealed; *i.e.* when carotene was high, vitamin *A* tended to be low, and *vice versa*. Individual variations between members of the same breed on the same diet were of the order of 100 per cent. When the carotene intake of the cow was increased there was an increase in both the carotene and vitamin *A*-content of the butter fat. Calculations indicated that 3·3 per cent. of the vitamin *A* ingested on a low carotene ration was secreted in the milk; on a high carotene ration only 1·3 per cent. was secreted. The results indicate that the proportion of the total vitamin *A* activity of butter due to carotene depends mainly upon the breed from which the butter is obtained. Vitamin *A* is of primary importance only in butter from those breeds which produce a butter of relatively low pigment-content. In a highly coloured butter most of the activity may be due to carotene. The results also emphasise the inadequacy of the natural colour of butter as an index of vitamin potency. P. H. P.

Differences between Biologically Active Substances before and after Isolation from the Raw Material in which they occur. H. I. Waterman and C. Van Vlodrop. (*Rec. Trav. Chim. Pay-Bas*, 1934, **53**, 670–671.)—Although it was found possible to recover carotene, dissolved in red or colourless palm oil, by distillation in a cathode light vacuum with internal condensation (*Rec. Trav. Chim. Pays-Bas*, 1933, **52**, 895), and consequently to concentrate solutions of carotene, yet when natural palm oil, or palm oil concentrate, was submitted to a similar treatment no concentration of colouring substances in the distillate could be obtained. However, the distillate from natural palm oil, on re-distillation under the same conditions, behaves like the carotene preparation dissolved in oil, the residue being freed to a large extent from the colouring substances. Concentration of the pigment practically without decomposition thus becomes possible. It is surmised that carotene does not occur as a free molecule in natural palm oil.

D. G. H.

Relation of Reducing Value and Extent of Browning to the Vitamin *C* Content of Orange Juice Exposed to Air. M. A. Joslyn, G. L. Marsh and A. F. Morgan. (*J. Biol. Chem.*, 1934, **105**, 17–28.)—It is known that orange juice exposed to atmospheric oxygen will gradually decrease in its reducing value towards iodine and also towards 2, 6-dichlorophenolindophenol; if the exposure is continued, browning occurs and increases in intensity. Studies were undertaken (i) to determine whether any change in vitamin *C* is involved in the browning of orange juice, and (ii) to compare the iodine titration with the indophenol titration as an indication of the changes in vitamin *C* content of orange juice during oxidative deterioration over a long period. Two lots of navel orange juice and one lot of Valencia orange juice were used, and it is shown that loss of vitamin *C* accompanies decrease in the iodine-reducing and indophenol-reducing value of orange juice, and occurs at about the same rate; the correlation of titre and antiscorbutic value is definitely better with Valencia than with navel orange juice. The extent of browning is parallel to the extent of loss in vitamin *C*, so that the latter is either involved in browning or it is destroyed simultaneously. Navel orange juice has a higher concentration of reducing substances than Valencia orange juice, and probably has more reducing material other than ascorbic acid; 1 ml. of navel orange juice is the equivalent of about 1·5 ml. of Valencia juice. The decrease in reducing value of orange juice which occurred during freezing storage was more marked in partly oxidised juice. There is little choice between the indophenol titration and the iodine titration for the determination of changes in vitamin *C*-content during prolonged oxidation of orange juice, but the iodine titration is easier to carry out and can be more readily duplicated. P. H. P.

Toxicological and Forensic

Spectrum of Haematoporphyrin and its Significance in the Recognition of Traces of old Blood-stains. M. Wagenaar. (*Pharm. Weekblad*, **1934**, **71**, 478–482.)—The fluorescence and spectroscopical properties of haematoporphyrin may be used as a means of identifying old bloodstains (*cf.* ANALYST, **1930**, **55**, 405). The action of sulphuric acid on the non-fluorescent haematin is to convert it into haematoporphyrin, which is fluorescent and appears purple in strongly acid solutions and dark violet in the presence of alkali. A fluorescence microscope and a micro-spectrometer are desirable for the study of small quantities of material. In the latter case a few threads are treated on a microscope slide with as much strong sulphuric acid as can be removed from the bottle on a straight platinum wire. A cover-slip is then placed in position, and a drop of acetone or of ethyl acetate is applied to its edge and allowed to flow under it. Local heating thus probably results, and both the extraction process and the formation of haematoporphyrin are stimulated and a good spectrum results (principal lines at 598 and 550$m\mu$); if a drop of ammonia is then drawn under the cover-slip by means of a strip of filter paper, the principal lines seen are at 615, 574, 544, and 509$m\mu$. J. G.

Organic Analysis

New Reactions of Aldehydes and Ketones. Synthesis of Thiodiazolines from Ketones. (Mlle) A. Lacourt. (*Bull. Soc. Chim. Belg.*, **1934**, **43**, 206–210.)—Aldehydes and ketones readily condense with thiohydrazides to form substituted thiodiazolines, which are easily purified. The reaction is general for aliphatic and cyclic ketones and acetophenones, but is given by benzophenones, camphor and fenchone so slowly that the thiohydrazide is decomposed by the prolonged action of the catalyst employed. When a solution of 3 grms. of α-phenyl-β (α-thionaphthyl)-hydrazine in 3 ml. of acetone is heated for 2 minutes with 10 drops of a 20 per cent. solution of hydrochloric acid in aqueous alcohol, 2:2′-dimethyl-3-phenyl-5-α-naphthyl-2:3-dihydro-1:3:4-thiodiazole, m.pt. 68° C., is formed. The other derivatives described were prepared similarly from: acetophenone and α-phenyl-β-phenylthioacetylhydrazine, m.pt. 120° C. (in 22 seconds); acetophenone and α-phenyl-β (α-thionaphthoyl) hydrazine, m.pt. 110° C. (20 secs.); cyclopentanone and α-phenyl-β-thiobenzoylhydrazine, m.pt. 94° C. (20 secs.); cyclopentanone and α-*p*-bromophenyl-β-thiobenzoylhydrazine, m.pt. 79° C. (20 secs.); cyclopentanone and α-phenyl-β (α-thionaphthoyl) hydrazine, m.pt. 98° C. (20 secs.). All of these heterocyclic derivatives dissolve in concentrated sulphuric acid, giving yellow or greenish-yellow solutions which, on addition of solid sodium nitrite, yield intense blue or violet colorations. Addition of a few drops of a 10 per cent. solution of silver nitrate in aqueous alcohol to saturated alcoholic solutions of the compounds gives a white precipitate; this usually begins to undergo reduction within a few minutes. T. H. P.

Detection of Carbon Tetrachloride in Chloroform. G. Ciogolea. (*J. Pharm. Chim.*, 1934, **126**, 377–383.)—Sivadjian's method (*ibid.*, 1929, **121**, 434) is satisfactory only when carried out exactly as follows: To a mixture of 5 ml. of a 1 per cent. solution of pyrocatechol in alcohol with 2 ml. of the chloroform in a test-tube, 0·5 ml. of sodium hydroxide solution (French Codex) is added so as to mix as little as possible with the alcoholic liquid. Powdered copper or commercial bronze powder (0·3 to 0·35 grm.) is then added, and the test-tube is heated for exactly 2 minutes in a water-bath at 100° C. The tube is at once cooled under the tap, 1 ml. of concentrated hydrochloric acid and 1 ml. of distilled water are added, the tube is shaken gently, and the liquid is allowed to stand for a few moments and then filtered. If the chloroform is pure, the filtrate is straw-yellow. If it contains from 0·25 to 0·5 per cent. of carbon tetrachloride, the colour is straw-yellow with a slight orange tint. With 0·5 to 1 per cent. of the tetrachloride, the filtrate is orange-yellow, and with more than 1 per cent., pink. A check test should always be made with anaesthetic chloroform. A modification of the method described in the French Pharmacopoeia (1908) is suggested, but this method cannot be made as sensitive as that given above. T. H. P.

Studies on the Merino Fleece. I. Chemistry of Suint. M. R. Freney. (*J. Soc. Chem. Ind.*, 1934, **53**, 131–134T.)—For the author's purposes, suint is taken to comprise those substances in raw wool which are soluble in warm water and are separated from the other elements of wool by simple filtration. Suint is normally neutral or slightly alkaline, but occasionally definitely acid, and different samples vary greatly in ash- and nitrogen-contents. From 10 to 20 per cent. of the dry matter consists of fatty acids, including lactic, hippuric, and succinic acids in small proportions. The nitrogen- and ash-contents of normal suint are similar to those of human sweat, but a dried sample of human sweat contained much more chloride than suint. No positive tests for proteins were given by suints or by human sweat. Small amounts of urea and ammonia occurred in most of the suint samples, the presence of nitrogenous bases suggesting that protein was originally present but had suffered decomposition. The inorganic constituents have not been thoroughly investigated, but one suint was found to contain much potassium, with less sodium and very little calcium. Sulphate, carbonate, chloride, silica, and traces of iron and phosphate were observed.

For two samples of suint from Australian merino wools, the following results were obtained on the dry matter:

Reaction	South Australian alkaline Per Cent.	Victoria neutral Per Cent.
Volatile acids	9·5	1·1
Higher fatty acids	2·0	13·8*
Organic matter { precipitated by lead acetate	—	24
Organic matter { not „ „ „ „	—	4·7
Ammonia	0·2	—
Hippuric acid	0·13	1·4
Total nitrogen	2·2	2·3
Succinic acid	—	1·4
Lactic acid	—	0·32
Ash	50	48

* Iodine value of these acids, 9·4.

T. H. P.

Inorganic Analysis

Determination of Small Amounts of Bismuth, Antimony, Tin, and Molybdenum in Copper (Spectrographic Method). B. Park. (*Ind. Eng. Chem., Anal. Ed.*, 1934, 6, 189–190.)—Bismuth, antimony, tin, and molybdenum, present in minute amounts in copper, may be quantitatively collected by co-precipitation on manganese dioxide from bromide-bromate solution, as follows: A 100-grm. sample of the copper is dissolved in 400 ml. of concentrated nitric acid, and the solution is evaporated to dryness on a steam-bath. The residue is dissolved in 1 litre of water, the solution is heated to boiling, and *N* sodium carbonate solution is added until a slight permanent precipitate is formed, which is then re-dissolved by the addition of 1 ml. of nitric acid. To the boiling solution are added 10 ml. of potassium bromide solution (20 per cent.), and 10 ml. of potassium permanganate solution (3 per cent.). The liberated bromine is removed by boiling for 30 minutes, and the precipitated manganese dioxide is filtered off and washed with a little water. The precipitate is combined with a second precipitate obtained by treating the solution with potassium bromide and permanganate as before, and dissolved in 50 ml. of concentrated hydrochloric acid. This solution is concentrated to 30 ml., neutralised with ammonia, acidified with 1 ml. of concentrated hydrochloric acid, diluted to 100 ml. and saturated with hydrogen sulphide. The sulphides are filtered off, washed with water, and dissolved in a hot mixture of 25 ml. of concentrated nitric acid and 10 ml. of hydrochloric acid. The solution obtained is evaporated to 5 ml., and 10 ml. of concentrated hydrochloric acid are added; the liquid is evaporated to 3 to 4 ml. and diluted to 5 ml. (Nothing is mentioned as to the possibility of loss of tin in these evaporations.—*Abstractor.*) The metals are determined by means of the arc spectrum of portions of the solution absorbed in graphite electrodes according to the method of Nitchie (*Ind. Eng. Chem., Anal. Ed.*, 1929, 1, 1). The fact that the precipitate obtained by a third treatment with bromide and permanganate of the copper solution, to which 2 mgrms. of each of the elements in question had originally been added, was spectroscopically free from them, was taken to prove the completeness of precipitation in the above method. Eleven different samples of refined copper gave the following results: Antimony, nil to 0·002 per cent.; tin, 0·00004 to 0·0015 per cent.; bismuth, $<$0·00001 to 0·0045 per cent.; molybdenum, nil to 0·0005 per cent. S. G. C.

Qualitative Separation of Cobalt from Nickel by means of Ammonium Phosphate. H. Wunshendorff and P. Valier. (*Bull. Soc. Chim.*, 1934, **1**, 85–90.)—Within a narrow range of p_H values and concentration of ammonium salts, cobalt phosphate is relatively insoluble, whilst nickel remains in solution. The following method is proposed for testing the mixture of cobalt and nickel sulphides obtained in the course of the qualitative group separations. The sulphides are dissolved in *aqua regia*, the solution is evaporated to dryness on a water-bath, and the residue is dissolved in the minimum of water. To a 2-ml. portion of the solution are added 1·5 ml. of 2 *N* ammonium carbonate solution, followed by 1·5 ml. of 2 *N* diammonium hydrogen phosphate solution. The liquid is heated to boiling and 20 drops of ammonia (sp.gr. 0·92) are added. The boiling is continued for 4 minutes, and the liquid is filtered without delay. If nickel is present, the filtrate is coloured a turquoise blue, and if cobalt is present, a violet precipitate remains on the filter. Quantities of the metals of the order of one-tenth mgrm. may thus be detected. S. G. C.

Separation of Potassium and Sodium as Iodides. L. Szebellédy and K. Schick. (*Z. anal. Chem.*, 1934, **97**, 106–116.)—The process is based on the solubility of sodium iodide and the insolubility of potassium iodide in a mixture of equal volumes of isobutyl alcohol and ether, both absolute. Chlorides and sulphates are converted into iodides by simple evaporation with hydriodic acid (sp.gr. 1·96); carbonates and nitrates are first converted into chlorides. Phosphates are not convertible, hence the phosphate ion must be removed by precipitation. The mixed salts (0·25 to 0·3 grm.) are dissolved in a few drops of water in a 50 ml. silica dish, and the solution is evaporated with hydriodic acid. The residue is dried for an hour at 125° C., cooled over sulphuric acid, and ground for 10 minutes with a small pestle under 5 ml. of isobutyl alcohol. Ether (5 ml.) is added, and the precipitate is left to settle for 3 minutes. The liquid is filtered through a small, close paper moistened with the alcohol. The insoluble residue is dissolved on the filter with 5 ml. of ethyl alcohol followed by 25 ml. of warm water. The washings are collected in the silica basin, and evaporated to dryness with a drop of hydriodic acid. The treatment of the residue is repeated, once if the mixture is poor, twice if rich, in sodium; if the potassium residue is small, the third extraction is carried out with 5 ml. of mixed solvent.

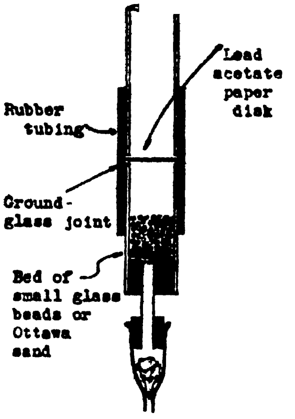
The sodium extract is evaporated to dryness in a wide, shallow weighing-bottle with ground-glass stopper, as sodium iodide is very hygroscopic. The salt must be dehydrated at 180° C. for one hour. Potassium iodide is not hygroscopic; it is dissolved in water, the solution is evaporated to dryness, and the residue dried like the sodium salt. The two alkalis may also be determined gravimetrically or volumetrically as silver iodide. In any case, a deduction of 0·0006 grm. is made from the calculated weight of Na_2O, and corresponding addition made to that of K_2O. If the amount of either alkali is very small, its identity should be proved. The advantages claimed are the direct determination of the sodium and the application to mixed sulphates after simple evaporation with hydriodic acid.

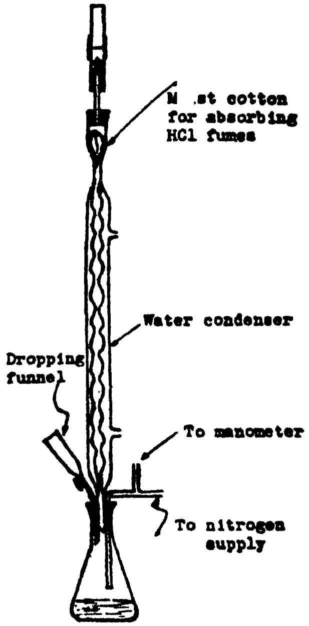
W. R. S.

Colorimetric Determination of Fluoride by means of a Photronic Colorimeter. L. V. Wilcox. (*Ind. Eng. Chem., Anal. Ed.*, 1934, 6, 167–169.)—Armstrong's method (*ibid.*, 1933, 5, 300), which involves the bleaching action of fluoride on the coloured ferric acetylacetone compound, has been used, a photronic colorimeter being employed for effecting the colorimetric comparison. The light-measuring elements of the colorimeter consist of two Weston Photronic cells, and the intensity of the light transmitted through the solution is measured in terms of electrical resistance. For the construction of the colorimeter, which is of a somewhat detailed character, and the method of working, the original paper should be consulted.

S. G. C.

Determination of Minute Quantities of Sulphide Sulphur. C. E. Lachele. (*Ind. Eng. Chem., Anal. Ed.*, 1934, 6, 200–201.)—The method involves the darkening of lead acetate-paper by hydrogen sulphide liberated by acid attack of the sample, an even degree of darkening of the paper being secured by allowing the gas to pass through a bed of sand or small glass beads before it reaches the paper. The sample is placed in the 1000-ml. flask of the apparatus (see Fig.), which is swept out with a stream of nitrogen; 50 ml. of hydrochloric acid (1 : 1) are added from the dropping funnel and the liquid is boiled, nitrogen being passed through it until all the sulphide has been evolved (time required is not stated). The lead





acetate paper is washed in distilled water and dried, and the stain is compared with standard stains obtained by evolving the sulphide from a suitable quantity of a standard steel. Pale stains may be compared in reflected light, but with darker stains examination in transmitted light is necessary. For amounts of sulphur between 0·008 and 0·08 mgrm., a lead acetate-paper disc 32 mm. in diameter is satisfactory; the accuracy is ±0·002 mgrm. *Applications.*—The method has been employed for the determination of sulphide sulphur in raw and canned foodstuffs (no details are given), water, the tin coating of tinplate and the sulphide stain imparted to the inside of tinned containers by certain foods. In the case of the stain, this was dissolved off without appreciable attack of the tin, by immersion of the sample for 2 minutes in a boiling solution consisting of 4 parts of sodium hydroxide solution (1 per cent.) and 1 part of sodium silicate solution (40° Bé.), and the sulphur was determined in this solution. For determining the sulphur-content of the tin coating of tinplate, the specimen was immersed in sodium hydroxide solution (1 per cent.), and sprinkled with pieces of cupric oxide wire. The tin coating, excluding the underlying alloy layer, dissolved off in about two hours at the ordinary temperature, or in a few minutes when the liquid was heated; the liquid, after the stripping process, was transferred to the apparatus for the evolution and determination of the sulphur. S. G. C.

Analysis of Phosphate-bearing Silicates. A. Lassieur. (*Ann. Chim. anal.*, 1934, 6, 197–202.)—When the proportion of phosphate is considerable, it is usual to effect the preliminary removal of phosphoric acid by precipitation as ammonium phosphomolybdate, and, as a consequence of this, it is necessary to eliminate the added excess of molybdenum remaining in the solution before proceeding with the determination of iron, aluminium, calcium, etc. The author recommends precipitating the iron, aluminium and calcium together by means of ammonium carbonate and ammonia, and removing the small quantity of entrained molybdenum in this precipitate by dissolving this in acid and precipitating with hydrogen sulphide. When the amount of phosphoric acid in the silicate is small, say, less than one-tenth of that of the iron and aluminium oxides present, it is possible to avoid the preliminary precipitation of the phosphate. The hydroxides of iron and aluminium may be precipitated with ammonia. The whole of the phosphoric acid is present in this precipitate as insoluble iron and aluminium phosphates, and calcium remains in solution. The precipitate is calcined, weighed, and taken up by fusion with potassium pyrosulphate; the iron oxide and phosphoric acid are determined in the solution obtained, and the aluminium oxide is found by difference. S. G. C.

Detection of Selenium and Tellurium. N. S. Poluektoff. (*Mikrochem.*, 1934, **15**, 32–34.)—(i) For the detection of selenium in the presence of tellurium, filter paper is treated with a drop of concentrated hydriodic acid (or potassium iodide solution and a drop of hydrochloric acid), and a drop of the acid test solution is placed in the middle of the moist fleck. If the black-brown fleck is then completely decolorised by sodium thiosulphate, no selenium is present. In the presence of selenium a red-brown fleck of elementary selenium remains. The limit of identification is 1γ of selenium (in 0·025 ml.), and the limit of concentration is 1 : 25,000. In the presence of tellurium the limit of identification is 2·5γ of selenium, and the proportion limit is Se : Te = 1 : 615.

(ii) Tellurium in the presence of selenium is detected as follows:—A drop of stannous chloride solution, a drop of 25 per cent. sodium hydroxide solution, and a drop of the alkaline test solution are mixed on a spot plate. In the presence of tellurous acid a black precipitate, or grey colour, appears. When very small amounts of tellurium are present the colour develops only after 1½ to 2 minutes, and a blank should be carried out. The limit of identification is 0·6γ of tellurium (in 0·025 ml.), and the limit of concentration is 1 : 41,000. For tellurium in the presence of selenium the limit of identification is 0·8γ of tellurium and the proportion limit is Te : Se = 1 : 100. J. W. M.

Determination of Selenium in Selenites, Selenates and in "Metallic Selenium." J. H. Van der Meulen. (*Chem. Weekblad*, **1934**, **31**, 333–335; *cf. ibid.*, 1931, **28**, 348.)—(i) *Reduction.*—A mixture of 20 ml. of a 0·05 *N* solution of sodium selenite with 150 ml. of water, 15 ml. of a 2 per cent. solution of starch, 10 ml. of *N* potassium iodide solution and 10 ml. of 5 *N* hydrochloric acid is titrated after 1 minute with a 0·1 *N* solution of sodium thiosulphate. If the above quantity of starch is added at an early stage, it serves as a protective colloid, and prevents precipitation of the reddish-violet elemental selenium

$$(Na_2SeO_3 + 4KI + 6HCl = 2NaCl + 4KCl + 3H_2O + 2I_2 + Se);$$

the end-point, which is a change from brownish-red to a brighter and purer red, is then sensitive to 1 drop of solution.

(ii) *Bromo-iodimetric Oxidation.*—The selenite is oxidised to selenate by means of hypobromite, the excess of which is determined (without reduction of the selenate) by liberation of iodine from an iodide in the presence of a catalyst and a strong acid; thus, $Na_2SeO_3 + NaOBr = Na_2SeO_4 + NaBr$. A mixture of 40 ml. of a 0·05 *N* solution of sodium selenite, 10 ml. of a *N* solution of potassium bicarbonate and 25 ml. of 0·2 *N* sodium hypobromite reagent (prepared by mixing solutions of 16 grms. of bromine in 500 ml. of water and of 12 grms. of sodium hydroxide in 100 ml. of water and diluting to 1000 ml.) is diluted with 50 ml. of water; a bicarbonate (or boric acid) ensures rapid and complete oxidation. The iodine liberated after addition of 10 ml. of a *N* solution of potassium iodide, 5 ml. of 5 *N* hydrochloric acid, and a few drops of a solution of a molybdate, is titrated in the usual way with a solution of sodium thiosulphate. (iii) *Selenium Metallicum.*—The powdered selenium (3·96 grms.) suspended in 100 ml. of water is treated with 8 grms. of solid potassium bromate, the reaction being stimulated, especially towards the end, by gentle heat and, in the final stages, by the addition of a further 2 grms. of bromate. The mixture is cooled and diluted to 1000 ml., and 20 ml. of this selenate solution are mixed with 20 ml. of 2 *M* potassium bromide solution and 10 ml. of hydrochloric acid. The selenate is thus reduced to selenite, which is determined (*cf. supra*) with potassium iodide and starch. The respective results (as percentages of Na_2SeO_3) for technical sodium selenite and *Natrium selenosum puriss.* for the 3 methods were:—(1) 93·55, 97·75; (2) 93·88, 98·00; (3) 93·55, 97·75. J. G.

Microchemical

New Method of Preparative Micro-chemistry. J. Winckelmann. (*Mikrochem.*, 1934, 14, 171–180.)—Permanent microscopic preparations of crystals and precipitates are made by covering the crystals with a thin film of collodion through which they can be washed without loss or disturbance, and finally mounting them in Canada balsam. The usual 6 per cent. collodion solution is used, or it may be diluted with a tenth of its volume of alcohol, or alcohol and ether. The method is illustrated by the formation and mounting of silver chromate. A small drop of 0·05 to 0·01 per cent. silver nitrate solution is placed on each of several clean microscope slides; one drop is left untouched, and to the others a trace of dilute nitric acid, or a trace of nitric acid and sodium or ammonium acetate is added. Then, into each of the drops is introduced a small crystal of potassium chromate. If the characteristic crystals appear at once, the solution contains too much silver, and the test should be repeated in greater dilution until a preparation is obtained in which not too many crystals are formed, and these are formed slowly and are well defined. The best preparation from the number of test drops is used for the final treatment. The drop is allowed to dry slowly until a crystal conglomerate of silver chromate and reagent is formed. This is covered with a thin layer of collodion, which may almost cover the whole slide. After this is dry a small drop of water (or wash liquid) is placed on the collodion over the preparation. The easily soluble salts soon dissolve and the drop can be removed by means of a small pipette with a rubber teat. This washing is repeated several times, and dilute alcohol may be used for the final washing. It is convenient to use a lens giving a magnification of about 10 during the washing. The drops of wash liquid must never be allowed to run over the edge of the collodion film, and, therefore, a level mounting table should be used. After washing, the preparation is allowed to dry in the air, and the excess collodion may then be cut away from the edges. The preparation is already fairly permanent, but it may be mounted under a cover glass and cemented with Canada balsam in the usual way. In this way permanent preparations are made for photography, or for measurement of size, crystal angle, and other physical properties. J. W. M.

Microchemistry of Euquinine. M. Wagenaar. (*Pharm. Weekblad*, 1934, 71, 435–438.)—Quinine ethyl carbonate ($C_2H_5O.COO.C_{20}H_{23}N_2O$) forms colourless and odourless crystals melting at 91° C., and having a slightly bitter taste; when dissolved in dilute sulphuric acid they give (like quinine) a solution having a blue fluorescence. Such solutions also give the thalleioquin reaction (green colour with bromine water and ammonia), and it is stated that this test is best made in an atmosphere of chlorine. Warm sodium hydroxide decomposes solutions of euquinine, with the liberation of ethyl alcohol, which may be detected by the iodoform test, a crystal of material being warmed with a drop of the alkali on a microscope slide just beneath a watch glass containing cold water which serves to condense the alcohol produced. An alternative, but less reliable, modification of the reaction is to warm the solution to be tested with ammonia and a solution of iodine in potassium iodide solution, when a yellow colour develops, and, after a time, crystals of iodoform are formed and may be identified under the microscope. Euquinine is best obtained for identification by slow evaporation of a solution in a mixture of acetone and water, from which it separates as characteristic, well-formed columnar crystals. Addition of a slight excess of ammonia to a solution of euquinine in dilute hydrochloric acid produces an opalescence which dissolves on addition of a few drops of acetone, and on evaporation of this mixture fine characteristic rosette-shaped crystals result. If one drop of a solution of iodine in potassium iodide solution is added to a solution of euquinine in dilute hydrochloric acid, an amorphous precipitate results which dissolves immediately on the addition of a drop of acetone and reappears in the form of fine crystalline bundles during slow evaporation (herapathite reaction).

J. G.

Collected References. Micro-Determination of Nickel and Cobalt. Z. Stary. (*Mikrochem.*, 1934, **15**, 141–150.)—The various methods for the micro-determination of cobalt and nickel are briefly described, and, in all, 53 references are given. The methods include: electrolytic, gravimetric (of which for nickel the most important is the dimethylglyoxime method), volumetric, colorimetric and spectrographic methods.

J. W. M.

Rapid Micro-method for the Determination of Uric Acid in Urine. P. Wenger, Ch. Cimerman and A. Maulbetsch. (*Mikrochem.*, 1934, **14**, 129–131.)—The usual macro-method, in which the uric acid is precipitated as ammonium urate, filtered, and determined by oxidation with $N/10$ iodine in alkaline solution, is carried out on 2 ml. instead of 100 ml. of urine. The Emich filter-stick, made of Berlin porcelain, is used for filtration. The sample is measured into a micro-beaker and treated with 6 drops of concentrated ammonia and 0·3 grm. of ammonium chloride, and, after standing five minutes, the mixture is filtered through the filter-stick, and the residue is washed three times with 1 ml. of wash liquid. The precipitate is washed down with 1 ml. of water and dissolved in acetic acid (1 : 10), added, drop by drop, until the solution is just acid. The filter-stick serves as a stirrer. After the addition of a little solid borax to render the liquid alkaline, the solution is titrated against $N/100$ iodine, starch being used as indicator. One ml. of $N/100$ iodine $\equiv$ 0·00084 grm. of uric acid, or n ml. $\times$ 0·42 + 0·01 = the quantity of uric acid in grms. per litre; 0·01 represents the correction for the slight solubility of ammonium urate. A determination can be completed in 15 minutes, as compared with 1½ hours for the macro method, and it gives equally accurate results.

J. W. M.

Micro-Determination of Urea in Blood. P. Wenger, Ch. Cimerman, and A. Maulbetsch. (*Mikrochem.*, 1934, **14**, 132–140.)—Fosse's method (*Compt. rend.*, 1913, **157**, 948; 1914, **158**, 1076, 1432) of precipitation of urea with xanthydrol, as modified by Nicloux and Welter (*Bull. Soc. Chim. biol.*, 1922, **4**, 128) for 1 ml. of serum is used, except that instead of the liquid being filtered through a micro-Neubauer crucible, an Emich filter-stick of Berlin porcelain is used. The filter-stick and micro-beaker containing the precipitate are dried in a Pichler drier at 105°–110° C., and finally weighed on a micro-balance. Accurate results are obtained. The Allen and Luck method (*J. Biol. Chem.*, 1929, 82, 696), in which titration replaces weighing was also used, but, instead of centrifuging the precipitate, it was filtered as before, using an Emich filter-stick. This simplifies the method and renders it more rapid, and the same degree of accuracy is obtained.

J. W. M.

Detection of Enzymes by "Spot" Tests. B. N. Sastri and M. Sreenivasaya. (*Mikrochem.*, 1934, 14, 159–160.)—The method consists in mixing on a strip of fat-free filter paper (3 in. × ½ in.) a drop of the substrate solution and a drop of the test liquid, and leaving the paper (together with the necessary controls) for 30 to 60 minutes in a moist atmosphere under a bell-jar. The drop is then examined for the reaction products with the suitable reagents. Where a reducing sugar is released, Fehling's test is used, and a jet of steam is directed on to the spot to facilitate reduction. A brick-red or orange colour indicates that the enzyme was present.

Enzyme	*Substrate*	*Reaction*	*Remarks*
Diastase	0·5 per cent. soluble starch	Fehling's	Brick red or orange colour
Inulase	0·5 per cent. inulin	Fehling's	,, ,, ,, ,,
Invertase	0·5 per cent. sucrose	Fehling's	,, ,, ,, ,,
Emulsin	0·5 per cent. salicin	Fehling's	,, ,, ,, ,,
Emulsin	0·5 per cent. indican	Treated with alkali and exposed to air	Blue colour
Lipase	0·2 per cent. olive oil emulsion	Methyl red	Red
Butyrase	0·2 per cent. ethyl acetate in aqueous emulsion	Methyl red	Red
Urease	1 per cent. urea	Phenolphthalein	Pink
Phenolase	1 per cent. tincture of guaiacum	—	Blue colour
Tyrosinase	Tyrosine	—	Brown

Amylase and urease are best detected on the spot plate, when a drop of 0·5 per cent. soluble starch and a drop of the test liquid are mixed and covered with a greased cover-slip. A number of the mixtures are made, and the colour reaction with iodine is examined from time to time. The urease test with phenolphthalein can be carried out similarly.

J. W. M.

Physical Methods, Apparatus, etc.

Use of Camphor in Cryoscopy for the Determination of the Molecular Weight of Arsinic Acids. C. Schuster. (*J. Pharm. Chim.*, 1934, 19, 497–498.) —Although the arsinic acids which are insoluble in the usual organic solvents are also insoluble in camphor (cryoscopic constant 500), the latter will dissolve derivatives similar in type to those formed by combination of compounds of arsinic oxides with thioglycollanilide (*cf. ibid.*, 1933, 17, 28), and may, therefore, be used for the determination of molecular weights. The procedure is to heat a mixture of 0·1 to 0·33 grm. of the sample with 1·4 to 2·3 grms. of camphor in a test-tube immersed in an oil-bath until the mixture melts, and, during cooling, to determine the depression of the crystallisation point to within 0·25° C. on continuous stirring with the thermometer. The following results for 5 out of the 9 compounds tested show the experimental and theoretical molecular weights, respectively; the former are calculated from Raoult's law, and correspond with freezing-point depressions of from 5·75 to 21·5° C.:—*p*-Chlorophenyl arsenite thioglycollanilide, 520, 518; *m*-nitrophenyl arsenite thioglycollanilide, 520, 525, 529; diphenyl arsenite thioglycollanilide, 381·5, 388·5, 385; phenyl arsenite thioglycollanilide, 477, 472. J. G.

Application of Absorption Spectra in Oil Research. Distillation of Palm Oil. L. J. N. Van der Hulst. (*Rec. Trav. Chim. Pays-Bas*, 1934, **53**, 672.)—A comparison of the absorption spectra of palm oil and of a solution of carotene in bleached palm oil, and of their distillates and distillation residues, respectively, confirms the investigations of Waterman and Van Vlodrop (see p. 498). The measurements were made between wave-lengths 380 to 520$m\mu$ and in the absence of interfering substances. Distillation of a solution of carotene in colourless palm oil gave a concentration of carotene in the distillate with a very small amount in the residue, whilst with natural palm oil only a small increase of carotene in the distillate was found. If palm oil in hexane solution is bleached with about 100 per cent. of bleaching earth (Terrana "superior") an oil is left with a spectrum similar from 220 to 500$m\mu$ to that of a mixture of oleic and stearic acids.

D. G. H.

Reviews

THE ATOM. By JOHN TUTIN, D.Sc. With an Introduction by Prof. FREDERICK SODDY, F.R.S. London: Longmans Green & Co. 1934. Price 6s. net.

We have travelled far since the publication of the fateful paper which heralded the opening of a new century, and marked the close of that comfortable era when an atom was but an extremely minute billiard ball whose behaviour could be predicted by a straightforward application of those Newtonian laws of mechanics which have been deduced from the observation of the behaviour of molar masses. It is remarkable that these concepts of large-scale mechanics should bear such a staggering extrapolation; and simple and naïve as this mechanical atom may be, the notion is not without its value to-day. But the complexities of radio-active phenomena demand a more complex atomic model, and the nuclear atom was supplied by Rutherford and quantised by Bohr, in accordance with the views that had developed since the appearance of Planck's pioneer paper just mentioned.

So far, matters were perfectly precise, and the notion of the atom was clear-cut, even though it might be steadily increasing in complexity. But now the growth of wave mechanics has forced us to replace this definite structure of a minute, complex, massive nucleus with its accompanying planetary orbits of electrons by a *probability pattern* the density of which at any point gives us a measure of the chance of finding an electron there. Our concept has become a trifle hazy at the edges. None the less, it fulfils the pragmatic test—it works.

Dr. Tutin would change all this; he inverts the atom and has his light electrons as part of the nuclear structure, with the heavy masses in orbital motion. As he himself naïvely remarks by way of illustration: "It may seem at first sight difficult to accept the alternative of very heavy masses spinning round a very light nucleus, but from the purely mechanical point of view there is nothing impossible in such an arrangement. On the contrary, a flywheel with a heavy rim and a light hub is a far more commonplace conception than a flywheel with a light rim and a heavy hub."

The book is not without interest, but Dr. Tutin will have to delve far more deeply than he does into the intricacies of modern spectroscopy if he wishes his ingenious atom to be taken seriously.

A. FERGUSON

PHYSICO-CHEMICAL METHODS. By J. REILLY, M.A., D.Sc., Sc.D., and W. N. RAE, M.A., F.I.C. Second revised and enlarged edition. Pp. xv + 882. London: Methuen & Co., Ltd. 1933. Price 42s.

Physical measurements are becoming of increasing importance in chemical work, and this is true no less of analytical and industrial laboratories than of those in which research work is the primary objective. The up-to-date analyst must not only be familiar with the determination of viscosities, of refractive indices and of hydrogen ion concentrations, but he is now expected to study absorption, Raman and X-ray spectra, and even measure dielectric constants. Until the appearance, in 1926, of the first edition of the volume under review there was no text-book available in the English language—apart from the elementary books suitable for undergraduates—by means of which chemists could make themselves familiar with the general outlines of practical physico-chemical methods. A definite need for such a work has been clearly proved by the fact that a new edition has been called for, in spite of its high price, in such a comparatively short time after its initial publication.

The present edition contains seventy-five chapters, divided into the following nine sections: Introduction; The Physical-Chemistry Laboratory and its Equipment; General Operations; Physical Measurements; Some Molecular Properties; Some Properties of Gases and Vapours; Thermochemistry; Optical Measurements; and Electrical Properties. The reviewer has been able to think of very few important measurements in chemistry involving physical methods which do not find mention in the book, although the authors "make no claim to completeness on account of the wide scope of the subject." In a future edition mention might well be made of the "rotation" method in X-ray spectroscopy, of the corrections for the capillary tube diameter in surface tension measurements, of the modern developments in the "moving boundary" method of transport number determination, and of the polarograph.

It is true that a large number of subjects are mentioned in the book, but the extent to which they are treated varies very considerably, and this variation may not always be to the taste of the reader; for example, the section on distillation occupies nearly forty pages, but the infra-red spectrometer is dismissed in three lines. Such inequality seems inevitable when only two authors attempt a comprehensive work of this nature, and until the ideal treatise on physico-chemical methods, written by a dozen or more specialists, is available, the book under review can be warmly recommended to all chemists.

S. GLASSTONE

A TEXT-BOOK OF INORGANIC CHEMISTRY. Edited by J. NEWTON FRIEND, D.Sc., Ph.D., F.I.C. Volume VI, Part II: PHOSPHORUS. By EDMUND B. R. PRIDEAUX, M.A., B.Sc., D.Sc., F.I.C. Pp. xxviii+238. London: Charles Griffin & Co., Ltd. 1934. Price 18s. net.

This exhaustive monograph bears abundant evidence of diligent compilation, especially of the physico-chemical data; the text is interspersed with numerous tables relating to densities, vapour pressures, conductivities, surface tensions, dissociation pressures, specific heats and volumes, etc., of the phosphorus compounds. The text is subdivided into fifteen chapters, dealing with the element; its allotropy; the phosphides; compounds with hydrogen, the halogens, sulphur, nitrogen; oxy- and thiohalides; oxides, unsaturated oxyacids, and the phosphoric acids. The concluding chapter discusses phosphatic fertilisers.

The preface is a brief but lucid survey of the important position of the element in agriculture and technology (phosphate industry and match manufacture), and of the rôle which the study of its compounds has played in the development of pure chemistry. The reader of this scholarly treatise, with its wealth of references to original papers on every page, will no doubt regret that the groups of the Periodic System described in the earlier text-books of Dr. Friend's series have not been accorded the same detailed treatment as is followed in the more recent ones. The eight members of the fourth group—including such elements of cardinal importance as carbon and silicon, the latter being dismissed in 56 pages—have been dealt with in 468 pages of text, whilst the four volumes devoted to the fifth group will aggregate 900 to 1000 pages by the time the last volume, now in preparation, is published. It is to be hoped that new editions of some of the parts will be re-written and enlarged. The reviewer can testify from personal experience that the treatment of the platinum metals is hardly adequate for more advanced study.

W. R. SCHOELLER

A TEXT-BOOK OF ELEMENTARY QUALITATIVE ANALYSIS. By C. J. ENGELDER, Ph.D. Second Edition. Pp. viii+243. London: Chapman & Hall. 1933. Price 13s. 6d.

The first edition of this text-book was reviewed in this journal (ANALYST, 1930, 55, 417). In the preparation of the present one the author has taken the opportunity to make some re-arrangement and extension of the subject-matter. Thus, a section is devoted to the electro-chemical oxidation-reduction theory and the equilibria existing in the corresponding systems, whilst Part II, dealing with the detection and separation of the cations, has been re-written and enlarged, with decided advantage from the point of view of the student. Several minor improvements have been made, with the result that certain reactions have been more clearly described, and a few of the newer tests for some metals have been introduced.

A new and desirable feature is the treatment of the binding of the book by pyroxylin impregnation to render it waterproof. Tests made on the cover with strong acids and alkaline solutions showed that no permanent damage resulted after an exposure of ten minutes, although glacial acetic acid removed a little of the red colour. This immunity suggests that, judging from the condition of the text-books belonging to certain students after brief use, it would be advisable to submit the whole of the pages to this reagent-proofing treatment.

The care expended in the proof-reading of this book is reflected in the almost complete absence of errors, the only ones detected being the addition of a final "n" to "chromium" on p. 144, and on p. 9 a mis-numbered reference to Tables XIX and XX, which should be XVIII and XIX.

Little evidence of the American source of this volume is shown, except in the transatlantic spelling of the names of a few elements. The general excellence of the first edition is maintained in the present one, and the book is well worth the attention of all engaged in the teaching of analytical chemistry.

T. J. Ward

Technical Gas Analysis. By George Lunge, revised and rewritten by H. R. Ambler, Ph.D. Pp. xvi+410, with 138 Figures and Diagrams. London: Gurney & Jackson, 33, Paternoster Row. 1934. Price 21s. net.

Twenty years ago the scientific public were fortunate in having so comprehensive a work upon gas analysis as that of Professor George Lunge. For many years it was the standard work upon the subject, and its very excellence is probably the reason why, despite the many advances in this science, it has not been challenged in its position of general supremacy. The revised edition, prepared by Dr. Ambler, must give general satisfaction, since it appears as an old friend, sufficiently up-to-date to satisfy the most modern of us and yet still in the old familiar form. The publishers and Dr. Ambler are to be congratulated upon having made so few alterations in the form and arrangement. They may even have gone too far in this direction by retaining the section upon gas analysis in acid and alkali manufacture. Chemical manufacture now covers a much wider field, and the special requirements of other industries might have been included.

The volume is divided mainly into general technique, volumetric methods, physical methods, methods for individual gas constituents and industrial applications.

The author rightly points out in the first place the importance of correct sampling. There are so many difficulties in obtaining a really representative sample that more space might well have been devoted to the procedure. Reliable methods of collecting average samples from both uniform and non-uniform seams should certainly have been fully described; at present references only are given.

The section on volumetric analysis deals first with the better-known types of apparatus, and then with the reagents necessary for the absorption of the different gaseous constituents. This is a comprehensive and useful section, and contains many references to literature where space does not permit of detailed description. The Bone and Wheeler apparatus is widely used in this country, and it is surprising that the author should illustrate on p. 70 the original form. The modified apparatus, which includes a copper oxide combustion tube and a reserve vessel for holding the residue for explosion, is much more useful. Fractional combustion of hydrogen and carbon monoxide is dealt with fairly fully, but would have been clearer if one apparatus had been shown in diagram. In the writer's experience many operators misuse the apparatus by employing unduly large volumes of reagent; the 5 ml. recommended by the author is much too large when one considers that the total volume of gas analysed is only from 10 to 20 ml.

The important question of the confining liquid in volumetric analysis is not dealt with fully. Mercury must generally be the recommended liquid, but there are occasions when water or certain solutions must be used. A table of solubilities of gas constituents in water, glycerin and water, calcium chloride solutions and certain reagents, would have been very useful, especially if related to a true factor.

The very considerable growth of physical methods is dealt with in a special section. Fractional distillation methods are well described; their importance has increased with the recent advances in the treatment of petroleum gas and in other catalytic processes.

Perhaps the most valuable section of the book is that dealing with special methods for the treatment of individual gases. The data given are conveniently cross-referenced to other sections of the book, and the information available is most comprehensive. There do not seem to be any omissions, although certain constituents could have been dealt with more fully than others. One of these is water vapour, the references regarding which are rather inadequate. Tables of equilibrium vapour pressures with the usual drying agents would have been helpful.

A volume such as this cannot deal adequately with so wide a subject as calorific value, but the principal methods of determining it are reviewed in a short section, and useful tables are provided for the calculation of calorific value from the results of analysis.

The use of devices for the automatic recording of the proportion of certain gaseous constituents is dealt with under flue gases, and a few of the proprietary apparatus are described. Such methods are so useful in the control of plant that this section might have been amplified by more complete descriptions and by the inclusion of methods for dealing with constituents other than those of flue gases. The Ranarex carbon dioxide recorder is little more than referred to, and the valuable Cambridge carbon dioxide and carbon monoxide recorder is not described at all.

The book is well printed in clear type and is freely illustrated. Both author and publisher are to be congratulated upon preserving the continuity of so old a friend as Lunge's Gas Analysis.

J. G. KING

THE DESIGN AND CONSTRUCTION OF HIGH-PRESSURE CHEMICAL PLANT. By HAROLD TONGUE. Pp. xi+420. London: Chapman & Hall. Price 30s.

Mr. Tongue's volume gives an excellent account of the technique of high-pressure chemistry as it is to-day. It is illustrated with a large number of excellent diagrams representing the high-pressure apparatus.

Since many chemical reactions involving gases take place with a decrease in volume, it is to be expected that the application of high pressures to gaseous reactions will be extended in the future. The working-out of a technique of high pressures was not alone sufficient to develop high-pressure chemistry. It was only the discovery of catalysts to enable the chemical reactions to take place under conditions in which the chemical equilibrium was over on the desired side, that caused the development of high-pressure chemistry. New catalysts are continually being discovered as they are required by the chemist and as high pressures are available to him.

The author devotes himself mostly to the science and practice of modern high-pressure methods, and gives only a short historical account of their development prior to 1910. He does not mention the first high-pressure laboratory in this country at Manchester, where Petavel and Hutton successfully installed plant in 1902 to work with gaseous pressures up to 200 atmospheres and temperatures up to those of the electric arc. There is no doubt that Haber used his knowledge of the work of Petavel and Hutton in first experimenting on the ammonia equilibrium at high pressures; and, later, Greenwood, who had learned this technique in Manchester, took it to Haber's laboratory and made accurate determinations of the ammonia equilibrium. The book can be recommended to all who may desire to use high pressures.

R. E. SLADE

Publications Received

A SUMMARY OF FOOD LAWS AND REGULATIONS. By C. L. HINTON. Pp. 90. London: The Nema Press Ltd. Price 21s. 0d.

THE NATURAL ORGANIC TANNINS. By M. NIERENSTEIN. Pp. 319. London: J. & A. Churchill Ltd. Price 21s. 0d.

ROAD MAKING AND ADMINISTRATION. By P. E. SPIELMANN and E. J. ELFORD. Pp. 441. London: Edward Arnold & Co. Price 25s. 0d. net.

AN ENQUIRY INTO THE NATURE OF CERTAIN NINETEENTH CENTURY PAMPHLETS. By J. CARTER and G. POLLARD. Pp. 400. London: Constable & Co. Ltd. Price 15s. 0d. net.

BRITISH ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE. REPORT OF THE ANNUAL MEETING, 1933.

THE ADSORPTION OF GASES BY SOLIDS. By S. J. GREGG. Pp. 120. London: Methuen & Co. Ltd. Price 2s. 6d. net.

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THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

New Apparatus for Determining the Temperature of Crystallisation of Cocoa Butter

(*Read at the Meeting, May* 2, 1934)

By S. A. ASHMORE, B.Sc., A.I.C.

The work here described was the outcome of a repetition of experiments by Bywaters and his collaborators (Analyst, 1927, **52**, 324), based upon the characteristic difference in behaviour of Borneo tallow and cocoa butter when allowed to cool without stirring. The temperature at which separation of solid fat occurs is a constant for each fat, and an apparatus has been devised whereby this temperature can be determined with precision and rapidity on as little as two grms. of fat. The Tyndall effect has been utilised by projecting a beam of light through a small tube containing the molten fat suitably housed in a darkened chamber; as soon as any separation of solid particles of fat takes place, a scattering of light occurs, and the tube containing the fat appears luminous against the darkened background. The temperature at which this is first seen is noted, and has been termed the crystallisation temperature; for cocoa butter it has proved to be a valuable criterion of purity. When applied to the examination of fats extracted from chocolate confectionery, of both home and foreign manufacture, its indications have been particularly useful in detecting Borneo tallow and certain other adulterants, the presence of which would not be indicated by the iodine value. The apparatus may have uses in other directions, and for this reason the present note has been communicated.

A diagram of the apparatus is shown in Fig. 1. It consists of a glass water-jacketed tube fitted with a cork through which pass a thermometer, and (to convey the light from a lamp to the centre of the apparatus) a piece of colourless glass rod bent as shown in the diagram. The end of the thermometer is surrounded by a small glass tube (1¾" × ⅜"), closed at one end. This contains the molten fat, and is attached to the thermometer by means of a rubber sleeve, so that the thermometer bulb is kept central. This small tube rests on a seating cut in another cork, which is also bored to take the glass rod; in this way the tube sits symmetrically over the end of the glass rod. With the exception of the tip, the glass rod inside the inner jacket is first covered with a layer of polished tin-foil, and over this is tightly secured a layer of black paper; this enables sufficient transmission of light through the rod to take place by internal reflection. The illumination is provided by a 60-watt "daylight" lamp suitably screened from the eyes; by adjusting the lamp against the outside end of the glass rod, a beam of light is led, by internal reflection, along the glass rod and projected upwards through the molten fat. The outside of the water-jacket is covered with a layer of black paper, and in this, a small observation window (indicated by the dotted rectangle in the diagram) is cut, so that the appearance of the fat on cooling can be noted.

In practice, when the fat is well above its crystallisation temperature, the appearance is as shown pictorially at 1 in Fig. 2. Apart from the thermometer bulb, an illuminated ring of light at the meniscus of the fat is all that can be seen in the darkened chamber. When the temperature has fallen to the point at which crystallisation is beginning, the solid particles of separated fat cause a scattering of the light, and the sides of the small tube can be seen faintly outlined, as at 2 (Fig. 2). This temperature, at which the mass is just uniformly turbid, is taken as the crystallisation temperature; the appearance, as indicated at 3 (Fig. 2), shows the tube strongly outlined by the light of the now numerous particles of separated fat. Condition 3, Fig. 2, occurs at a temperature 0·2 to 0·4° C. lower than that at which condition 2, Fig. 2, is noted. It will thus be seen that the onset of crystallisation is well defined, and independent observers have had no difficulty in agreeing within about 0·2° C. on the temperature of crystallisation indicated by the appearance at 2, Fig. 2.

It is, of course, essential that the fat should be perfectly clear and bright in the molten condition, and for the small amounts of fat extracted from chocolate, a filtering device working on the syringe principle, and having a plug of filter paper in the nozzle as filtering medium, has been adopted. The filtered fat is kept in a water-bath at 40° C. for several minutes to ensure that it is in a thoroughly molten condition, and while at this temperature it is introduced into the inner jacket, the air of which is kept at a steady temperature of 18° C. by the circulation of water through the outer jacket. The determination of the point at which crystallisation first begins is facilitated by fitting a small black cardboard hood over the observation window, and by suspending a large sheet of black paper behind the apparatus to give a darkened background.

In order to establish the range of crystallisation temperature for genuine extracted cocoa butter, a quantity of the fat was extracted from a number of cocoa nibs previously handpicked free from shell and germ. The fat was extracted in the usual way with petroleum spirit, and, after removal of the solvent, was filtered. The following results were obtained:

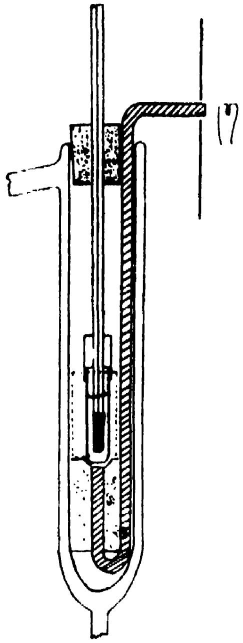

Fig. 1

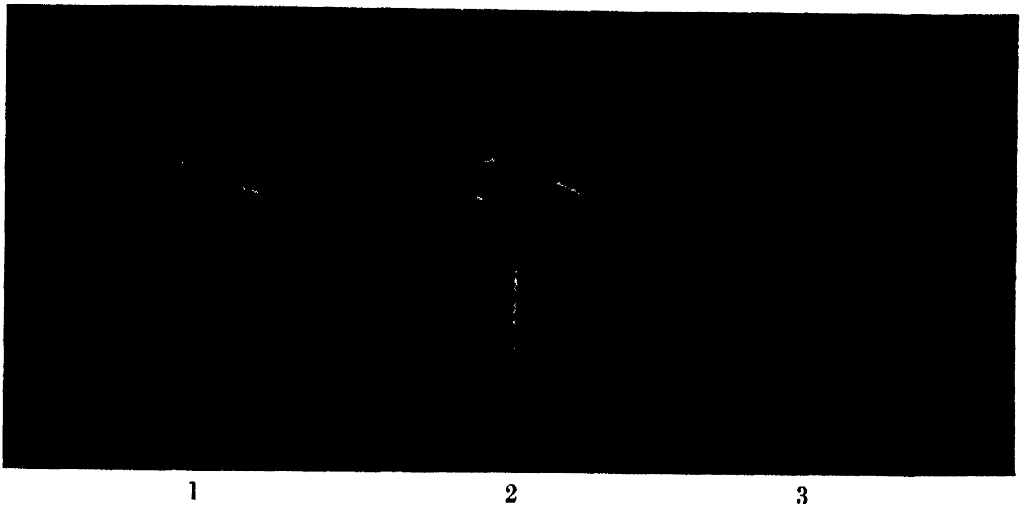

Fig. 2.
Determination of Crystallisation Temperature

Source of cocoa butter	Crystallisation temperature °C.
Accra nibs	20·0
Arriba ,,	20·7
Carácas ,,	20·3
Trinidad ,,	20·8
Java ,,	20·3

Shell butter causes a slight lowering of the crystallisation temperature.

Examination of mixtures of Borneo tallow and cocoa butter gave the following results:

Borneo tallow Per Cent.	Cocoa butter Per Cent.	Crystallisation temperature Observer 1 °C.	Crystallisation temperature Observer 2 °C.
0	100	20·2	—
20	80	22·0	21·8
40	60	24·0	24·0
50	50	24·8	24·8
60	40	27·0	—
70	30	28·5	—
80	20	29·5	29·4
100	0	31·2	31·4

I wish to acknowledge the help received from Mr. A. A. Russell and Mr. V. H. Field, and to thank the Government Chemist, Sir Robert Robertson, for permission to publish this note.

Government Laboratory
Custom House, E.C.3

Detection of Diamines in Leather

By WILFRED MATHER, A.M.C.T., F.I.C., and WILLIAM J. SHANKS, A.M.C.T.

(*Read at the Meeting, April 4, 1934*)

The detection of diamines was a part of the work covered by Cox (Analyst, 1929, 54, 694) in his examination of dyed furs. Forster and Soyka (*J. Soc. Dyers & Col.*, 1931, 47, 99) investigated the fate of the dyestuff intermediates in the dyeing of furs, and extended the reactions for the detection of the diamines.

Immediately afterwards, analysts used these reactions, especially Cox's tests, for the detection of diamines and amino-phenols in dyed and finished leathers, and sometimes reports were issued showing the presence of *p*- and *m*-phenylene-diamines, even in undyed leathers. When the published tests for the detection of diamines in leather were used, attention was not given to the fact that the tannins present in the leather were capable of interfering seriously with the tests and, in some of the tests, of confusing or even simulating the reactions produced by diamines.

Callan and Strafford (ANALYST, 1931, **56**, 625) studied the detection of diamines in the presence of tannins, and made a further extension of Cox's tests. They added diamines to the extractives made by submitting the leather to 48 hours' extraction with 1 per cent. acetic acid.

Humphreys and Phillips (ANALYST, 1932, **57**, 290) advanced the work by adding known quantities of diamines to leathers and extracting the diamines with acid solutions. These acid extractives were freed from tannin by re-extracting them with benzene, the tannins being soluble in the benzene, whilst the diamine hydrochlorides were left in the aqueous acid portion. A conclusion drawn by Humphreys and Phillips was that leathers containing meta-diamines did not show the test for those diamines in the acetic acid extracts, but did so in hydrochloric acid extracts. We find, however, that 1 per cent. acetic acid does extract diamines from leather in two hours in the cold.

In Callan and Strafford's work the diamines were added to the leather extract, so that the tests were not carried out on leathers actually containing diamines. Up to the present, therefore, we consider that there is no published method capable of quickly detecting diamines in leathers containing tannin, and we are pleased to be able to publish tests which we have devised and used for some considerable time. Our first aim was to find a method of getting rid of the interfering and masking effects of the tannins in the acid extract of the leather, and precipitation of the tannins with lead acetate solution was found to be an effective means of doing this. This operation, and the subsequent removal of the excess of lead acetate from the filtrate by means of ammonium sulphate, does not interfere with the diamines originally extracted from the leather.

With the exception of the indamine reaction, which was not found completely successful in the presence of excess of tannin, all the tests for diamines previously advanced give rise to red, brown, or yellow colour reactions, and seem to show results differing in degree rather than kind.

We therefore endeavoured to devise tests which, while readily giving sharp colour changes, would also be capable of detecting small quantities of diamines. After producing satisfactory tests capable of giving fair results in the presence of tannin, we evolved the method whereby the influence of tannin could be overcome by means simpler than extraction with benzene.

METHOD.—The details of the method used in our laboratories for some considerable time are as follows:—Three grms. of leather are cut up into strips and extracted in a beaker for 2 hours with 30 ml. of *N*/10 hydrochloric acid in the cold. The extract, which is usually coloured, is then decanted, and 10 ml. are treated with excess of lead acetate solution to precipitate the tannin. The lead tannate is filtered off, and the filtrate is tested with a drop of lead acetate solution to establish complete removal of the tannin. The excess of lead acetate in the filtrate is removed by addition of ammonium sulphate solution, the lead sulphate is filtered off, and the filtrate is made up to 20 ml.

This treatment of the leather extract does not interfere with any diamine which may be present, as can be shown by adding a small quantity of diamine to a tannin solution before proceeding to precipitate the tannins with lead acetate solution.

DETECTION OF META-DIAMINES.—Four ml. are made slightly alkaline with ammonia, 1 drop of a 0·1 per cent. solution of dimethyl-*p*-phenylene-diamine hydrochloride is added, and the tube is well shaken. Four drops of 0·1 per cent. potassium dichromate solution are added, and the tube is again well shaken, after which the solution is acidified with acetic acid and well shaken, and any colour change is noted (*a*). The solution is next warmed on the water-bath to 50° C., and the change in colour is noted (*b*); afterwards the liquid is boiled for two or three minutes, and the colour change is noted (*c*). If metaphenylene-diamine or metatoluylene-diamine is present, the observations are:—(*a*) slowly turns blue; (*b*) pronounced blue; (*c*) deep red. Paraphenylene-diamine, dimethyl-paraphenylene-diamine, para-amino-phenol, and methyl-para-amino-phenol do not give these reactions.

In a treated tannin solution this test is capable of detecting 0·0004 per cent. of metaphenylene-diamine or 0·0002 per cent. of metatoluylene-diamine.

DETECTION OF PARAPHENYLENE-DIAMINE.—*A*. Four ml. of the lead-treated leather extract are treated as for the detection of meta-diamines, 4 drops of 0·1 per cent. solution of dimethylaniline hydrochloride being used, instead of the dimethyl-*p*-phenylene-diamine solution.

If paraphenylene-diamine is present in the leather extractive, the colour changes are:—(*a*) greenish; (*b*) green; (*c*) green.

If dimethylparaphenylene-diamine is present, the colour changes are:—(*a*) pink changing to purple; (*b*) blue changing to green; (*c*) green.

Metaphenylene-diamine, metatoluylene-diamine, para-amino-phenol, and methyl-para-amino-phenol do not give these reactions.

This reaction is capable of detecting 0·0001 per cent. of paraphenylene-diamine in a treated tannin solution.

B. Four ml. of the lead-treated leather extract are treated as in *A* (detection of paraphenylene-diamine), 4 drops of 0·1 per cent. solution of aniline hydrochloride being used, instead of the dimethylaniline hydrochloride. If paraphenylene-diamine is present in the leather extract, the colour changes are:—(*a*) green; (*b*) blue; (*c*) red.

If dimethylparaphenylene-diamine is present, the colour changes are:—(*a*) pink changing to purple; (*b*) blue changing to green; (*c*) green.

Metaphenylene-diamine, metatoluylene-diamine, para-amino-phenol, and methyl-para-amino-phenol do not give these reactions.

This reaction is capable of detecting 0·0002 per cent. of paraphenylene-diamine in a treated tannin solution.

The following table summarises the results obtained in the tests:—

Reagent	Temp.	Leather containing no added diamine	Leather containing 0·05 per cent. meta-phenylene-diamine	Leather containing 0·05 per cent. para-phenylene-diamine	Leather containing 0·05 per cent. meta-toluylene-diamine	Leather containing 0·05 per cent. dimethyl-para-phenylene-diamine	Leather containing 0·05 per cent. para-amino-phenol	Leather containing 0·05 per cent. methyl-para-amino-phenol
Dimethyl-para-phenylene-diamine (0·1 per cent. solution)	Normal	Orange-red	BLUE	Orange-red	BLUE	Orange-red	Orange-red	Orange-red
	50° C.	Light red	DEEPER BLUE	Light red	DEEPER BLUE	Light red	Light red	Light red
	Boiled	Yellow-brown	DEEP RED	Yellow-brown	DEEP RED	Yellow-brown	Yellow-brown	Yellow-brown
Dimethylaniline (0·1 per cent. solution)	Normal	Yellow	Yellow	YELLOW-GREEN	Yellow	YELLOW	Yellow	Yellow
	50° C.	do.	do.	GREEN	do.	YELLOW-GREEN	Yellow-orange	Orange
	Boiled	do.	do.	DEEPER GREEN	do.	GREEN	Orange	do.
Aniline (0·1 per cent. solution)	Normal	Yellow	Yellow	GREEN-BLUE	Yellow	YELLOW	Yellow	Yellow
	50° C.	do.	do.	BLUE	do.	GREEN	do.	do.
	Boiled	do.	do.	ORANGE-RED	do.	ORANGE-RED	do.	do.
Ortho-toluidine (0·1 per cent. solution)	Normal	Yellow	Yellow	BLUE	Yellow	YELLOW	Yellow	Yellow
	50° C.	do.	do.	BLUE	do.	GREEN	do.	do.
	Boiled	do.	do.	RED	do.	ORANGE-RED	do.	do.
Para-phenylene-diamine (0·1 per cent. solution)	Normal	Yellow	PURPLE	Yellow	PURPLE	Orange	Yellow	Yellow
	50° C.	do.	PURPLE	do.	RED-PURPLE	do.	do.	Orange-yellow
	Boiled	Brown-yellow	RED	Brown-yellow	RED-PURPLE	do.	Orange-yellow	do.
Meta-toluylene-diamine (0·1 per cent. solution)	Normal	Yellow	Yellow	PURPLE	Yellow	GREEN	Yellow	Yellow
	50° C.	do.	do.	PURPLE	do.	BLUE	Orange-yellow	Orange-yellow
	Boiled	Orange-yellow	Orange-yellow	RED-PURPLE	Orange-yellow	ORANGE-RED	Orange	Orange

The reactions shown in this Table are the same for both undyed and dyed vegetable-tanned leather.

CHROME-TANNED LEATHERS.—When diamines are present in chrome-tanned leather they can be detected by the same tests as those used for vegetable-tanned leather. The diamines are extracted with $N/10$ hydrochloric acid, and, inasmuch as there are usually no free vegetable tannins present, the tests can be carried out on the hydrochloric acid solution directly, that is, without treatment with lead acetate, etc.

To illustrate this, the following types of chrome-tanned leathers were tested:—*A*. Full-chrome lambskin, for glove leather, undyed; *B*. full-chrome lambskin, for glove leather, dyed; *C*. semi-chrome Persian, for glove leather, undyed; *D*.

semi-chrome Persian, for glove leather, dyed; *E.* semi-chrome sheep, for clothing, dyed black and finished with black pigment.

In each instance the leather was damped on each side with a solution of diamines and made to take up 0·02 per cent. of the diamine. The samples were then completely dried overnight, and on the following day they were extracted with *N*/10 hydrochloric acid and tested as described.

In every instance diamines were detected and identified by means of the colour reactions given in the table.

SUMMARY.—Tests have been worked out whereby para- and meta-diamines can be detected in dyed and finished leathers when present in extremely small quantities. Paraphenylene-diamine can be detected when present to the extent of 0·005 per cent. in the leather; metaphenylene-diamine when present to the extent of 0·017 per cent.; and metatoluylene-diamine to the extent of 0·01 per cent. These will be seen to be small quantities when it is realised that a hat leather weighs 10 to 12 grms., and has a surface area of 50 square inches on each side.

Furthermore, the tests are capable of showing that the para- and meta-diamines are extracted from leather in the cold by 2 hours' extraction with *N*/10 hydrochloric acid or 1 per cent. acetic acid solution, and that the interfering influences of the tannins present in the leather can be removed by simple means.

MESSRS. ROBERT NOBLETT, LIMITED
LEATHER WORKS, AUDENSHAW, NR. MANCHESTER

DISCUSSION

DR. H. E. COX said that the paper was a valuable contribution to a difficult subject; he must, however, disclaim any responsibility for the mis-use of the tests in his paper to which the authors had referred. It seemed to him an elementary precaution in dealing with a supposed dyed leather to determine whether or not it really was dyed, and if it was, with what class of dyestuff. He thought that, in general, it was better to extract the diamine in a fairly pure state as suggested by Humphreys and Phillips, rather than to use precipitation methods. The reactions shown by the authors appeared to be variations of the well-known indamine test, and the indamines, on heating, produced safranine or analogous substances which were, no doubt, responsible for the red colours shown on boiling.

MR. C. E. SAGE mentioned that different parts of skins had to be examined. He had to deal with fur, and with the leather. On the skins used for making suede shoes it was not only the dye used by the manufacturer of the leather, but also the substances used in the various preparations for renovating or cleaning them which might be a source of danger to the wearers.

A Rapid Qualitative Test for Ethylene Glycol and its Application in the Presence of Glycerol

By A. W. MIDDLETON, B.Sc., A.I.C.

(*Read at the Meeting, April* 4, 1934)

During the last few years the use of the higher fatty acid esters of ethylene glycol and of glycerol as soap substitutes and emulsifying agents has been developed in America and on the Continent. The analyst confronted with the investigation of a product possibly containing esters of one, or both, of these alcohols has no ready means of identifying the glycol in the presence of glycerol. Such a test would enable him to place more reliance on the interpretation of his glycerol result; the usual chemical determination of glycerol depends on the determination of hydroxyl groups either by acetylation or by oxidation. Three molecules of a glycol ester differ from two molecules of a corresponding glycerol ester only in that they contain two hydrogen atoms more, and this slight difference might not be detected in the ordinary course of commercial analysis. To differentiate between the esters or mixtures of them it would be necessary to isolate them or their alcohols, in a pure state—a tedious and expensive undertaking. Hence an attempt was made to find a rapid test for ethylene glycol suitable for application in the presence of glycerol.

There is scant literature on the detection of glycol. B. Müller (*Chem.-Ztg.*, 1920, **44**, 513), who was not concerned with their differentiation, applied the methods of determining glycerol to glycol. He found that the acetin and dichromate methods, and the method of weighing the carbon dioxide formed on oxidation with a mixture of sulphuric acid and chromium trioxide, give as good results with glycol as with glycerol. Fleury and Marque (*J. Pharm. Chim.*, 1920, **10**, 241) based a method of determination on the oxidising action of alkaline mercuric iodide and potassium iodide on the hydroxyl groups in glycol, glycerol, and other polyols. The reaction is not strictly quantitative, but it was found useful for the determination of glycol, mannitol, inositol, and dulcitol. Wolff (*Chem.-Ztg.*, 1917, **41**, 608) studied Denigès' tests for glycerol, in which he oxidised the alcohol with alkaline bromine, removed the excess of bromine, and then added solutions of various phenolic substances which give coloured bodies with the aldehydic decomposition products from the glycerol. He found that technical glycol and glycerol gave similar colours, and that these colour-tests had no differential value. He suggested the determination of the refractive index of the alcohols as a rough means of deciding the extent of admixture. Thomas and Micsa (*Chem. Zentr.*, **136**, [i], 1925) used R-acid as a reagent for polyhydroxylic alcohols. This reagent, after oxidation of the alcohols by bromine water, ultimately gives with glycol a blue colour surrounded by a yellow ring, and with glycerol a greenish-blue colour surrounded by a yellow ring. Other polyhydroxylic alcohols and aldehydic bodies give intensely coloured products. Alber (*Mikrochem.*, 1929, **7**, 21) reviewed the microchemical reactions for glycol, glycerol, and mannitol, and found that a modified Denigès' test involving the use of β-naphthol and "layering" with sulphuric acid, as described by Fischer and Tafel (*Ber.*, 1887, **20**, 3384), was the only useful method of differentiation. Glycol gives a reddish-violet and glycerol a green colour when the pure alcohols are used. Wolff (*loc. cit.*), who used technical glycol, found the β-naphthol test not so satisfactory.

None of these methods for the determination or detection of glycol is practicable in the presence of glycerol. With those that give a coloured solution as their end-point, the difference between glycol and glycerol is slight, and does not permit of their detection when mixed together. The methods of Fleury and Marque, and of Müller are dependent on the determination of the hydroxyl groups in the molecule, and are hardly suitable for differentiation between the various polyhydroxylic alcohols.

From an examination of the reactions of these alcohols (Beilstein; Richter; J. M. Lawrie, *Glycerol and the Glycols*, Chem. Catalog. Co.), oxidation appears to be a suitable basis for a rapid qualitative test. Moderate oxidising agents convert glycerol into glycerose, whilst more energetic oxidation causes complete decomposition into carbon dioxide and water. With glycol, moderate oxidising agents give oxalic acid. Chief among these is nitric acid, giving aldehydic bodies from glycerol, oxalic acid from glycol, and yet only slowly oxidising oxalic acid itself to carbon dioxide and water. As oxalic acid is readily detected, a test was tried which was based on the oxidation of the free alcohols by nitric acid, followed by the examination of the decomposition products for oxalic acid.

It was decided to use a 10 per cent. aqueous solution of the alcohol in all experiments. This would prevent too much loss of alcohols by evaporation during the concentration of their solution after saponification of the esters and removal of the fatty acid portion (*i.e.* by the method necessary to obtain the alcohol in the ordinary course of analysis). After a few preliminary results the following was adopted as an initial procedure:

Two ml. of nitric acid (sp.gr. 1·42) were added to 10 ml. of the solution, and the mixture was evaporated to approximately 1 ml. in a small evaporating basin. Five ml. of 20 per cent. w/v ammonium chloride solution were then added, and the dish was allowed to cool. The liquid was made slightly alkaline by adding, 1 ml. at a time, 10 per cent. sodium hydroxide solution, until there was a slight smell of ammonia, after which the solution was boiled until neutral, *i.e.* until no odour of ammonia could be detected. One ml. of 10 per cent. w/v barium chloride solution was next added and, after about 15 minutes (during which time the liquid was cooled in a bath of cold water), the precipitate was filtered off on a No. 40 Whatman filter paper and washed with about 5 ml. of water, *i.e.* until the filter paper was nearly stain-free. The precipitate was then rinsed into a boiling-tube by means of 5 ml. of water, 7·5 ml. of 2 *N* sulphuric acid were added, and the mixture was heated just to boiling-point. The resulting oxalic acid solution was cooled and filtered from the barium sulphate through a Whatman No. 40 paper. The filtrate was treated with 0·6 *N* potassium permanganate solution until no more was decolorised *in the cold*; usually there was no decolorisation, and if decolorisation occurred it was regarded as being due to decomposition products other than oxalic acid. The solution was then boiled, and any further decolorisation of the potassium permanganate was regarded as showing the presence of oxalic acid, and hence the initial presence of glycol.

The experimental results relate chiefly to variations of the procedure in order to obtain the optimum conditions for the test. Experiments were then made to determine the rough limits of sensitivity of the test. When a large proportion of glycerol was present and the solution was boiled for a considerable time with the alkali, it gave a brown colour, but this brown colour could be readily removed by washing the subsequently precipitated barium salt. It was found that 1 grm. of glycerol gives no oxalate precipitate, whilst 0·1 grm. of glycol will give a positive result; yet, in the case of a mixture, this amount of glycol cannot be detected, and at least 25 per cent. of the alcohols present must be glycol in order to obtain a definite reaction for that substance.

Experiments were then made in which the different points of the procedure were varied singly. The results, all on an aqueous solution of 0·2 grm. of glycol in 10 ml. of water, showed that the procedure could not be improved; that the use of too much nitric acid interfered by precipitating barium nitrate with the oxalate; and that the solubility of barium oxalate necessitates that the bulk of the solution should be kept as low as possible at the neutralisation stage.

Other experiments definitely established the interfering effect of glycerol. It was found that in its presence quite considerable amounts of glycol could not be detected, while blanks showed that the test was still quite sensitive to glycol in the absence of glycerol.

Attempts were made to rectify this effect of the glycerol, but they were not successful. The glycerol used was free from the heavy metals most likely to catalyse the oxidation of the oxalic acid by nitric acid. Alteration of the speed of evaporation of the nitric acid and alcohol mixture, from which the glycol might boil off in the presence of glycerol, did not seem to give any improvement; neither did increasing the concentration of the sodium hydroxide from 10 to 20 per cent., with a consequent reduction in the bulk of the liquid from which the barium oxalate was precipitated. Fuming nitric acid (sp.gr. 1·5) was of no use, as it gave positive results with glycerol in the absence of glycol. Evaporation of the oxidising liquid to 0·5 ml. gave better results in some cases, but the results were unreliable.

Thus the test developed can be used for the detection of glycol alone and for mixtures of glycol with glycerol containing up to 75 per cent. of the latter. It is sensitive to 0·1 grm. of glycol in 10 ml. of aqueous solution, and will detect as little as 0·3 grm. of glycol in the presence of 0·7 grm. of glycerol in 10 ml. of aqueous solution.

At the suggestion of Dr. H. E. Cox, attempts were made to adapt the test to the detection and determination of trimethylene glycol in the presence of glycerol, but the results were very unsatisfactory; the method is not applicable to trimethylene glycol.

I wish to thank Dr. A. M. Ward for his interest and helpful criticism.

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A Rapid Test of Thickness of Tin Coatings on Steel*

BY S. G. CLARKE, B.Sc., PH.D., A.I.C.

THE methods at present available for the determination of thickness or weight per unit area of tin coatings on steel involve chemical analysis, the test specimen being dissolved in acid, and the tin present in the solution in the stannous condition being titrated with a standard oxidising solution. These methods are capable of yielding accurate results, but their usefulness for inspection purposes is limited. Thus, whereas chemical analysis records the total tin present on an article, it is frequently desired to determine the thickness of tin on a particular portion of the surface such as, for example, one side only of a tinned sheet. Further, with specimens other than thin sheet, dissolving the specimen for chemical analysis may occupy considerable time, and there is the possibility of interfering matter being dissolved from the basis metal; alternatively, where the basis metal is not completely dissolved, there may be uncertainty as to the completeness with which the tin coating is dissolved. Owing to the readiness with which bivalent tin is oxidised by the air, it is desirable to use an apparatus in which the dissolved tin can be kept in an inert atmosphere until the titration is completed.[1]

It appeared that a method in which the tin coating could be selectively dissolved off and determined by loss in weight of the specimen might offer advantages. A method of this type is already available for electro-deposited cadmium coatings on steel,[2] in which cold hydrochloric acid containing antimony chloride is employed for dissolving off the cadmium without appreciable attack of the steel. It has now been found that tin also dissolves readily in this solution, rendering possible an extension of this stripping method to tin coatings on steel.

DESCRIPTION OF METHOD.—*Solution required.*—Twenty grms. of antimony trioxide (Sb_2O_3) dissolved in 1 litre of cold hydrochloric acid (sp.gr. 1·146).

Procedure.—(*a*) *Determination of tin on total area.*—The article to be tested, after being freed from grease by treatment with a grease solvent and weighed, is immersed in the solution. When the evolution of gas has ceased, the article is allowed to remain in the solution for a further period of 1 minute. It is then withdrawn, washed without delay in water, mopped with a wet soft cloth or cotton-wool swab to remove black powdery deposit, dried and weighed. The area from which the tin has been removed is measured.

(*b*) *Determination of tin on selected area.*—The degreased and weighed specimen is coated with Necol varnish† applied by means of a brush (the selected area being left uncoated), and allowed to dry for 15 minutes. The tin coating is then removed from this area by immersion as in (*a*). After being washed with water, the Necol film is removed by rubbing with a cotton-wool swab saturated with acetone, in which the film is readily soluble; the article is finally washed with acetone, allowed to dry, and weighed. This method is suitable for determining the amount of tin on one face of tinplate sheet or as an alternative to cutting up articles which are not too large for weighing.

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* Communication from the Research Department, Woolwich.

† A cellulose varnish supplied by Imperial Chemical Industries, Ltd.

Calculation of results.—The thickness of coating may be calculated with the aid of the following formulae:

$$\mathrm{T\ (inch)} = \frac{\mathrm{W\ (grm.)}}{\mathrm{A\ (sq.inch)} \times 118} \text{ or } \mathrm{T\ (cm.)} = \frac{\mathrm{W\ (grm.)}}{\mathrm{A\ (sq.cm.)} \times 7{\cdot}2}$$

T = thickness; W = weight of coating; A = area of coating.

It has been found that the following corrections should be applied to the calculated thickness:

(*a*) hot-dipped coatings: 4×10^{-6} inch (1×10^{-5} cm.) to be deducted.

(*b*) electro-deposited coatings: 1×10^{-6} inch ($2{\cdot}5 \times 10^{-6}$ cm.) to be deducted.

The weight of tin found may be converted into the customary trade units[3] from the relation 0·1 grm. per 100 sq.cm. of surface = 14·5 ounces per base box, the appropriate correction to be deducted being 1 ounce per base box for a hot-dipped coating. One lb. of tin per base box is approximately equivalent to a thickness of 6×10^{-5} inch ($1{\cdot}5 \times 10^{-4}$ cm.). With the hot-dipped coatings, the result obtained is inclusive of the tin present in the alloy layer.

Notes.—For routine testing of tinned sheet steel, a test-specimen measuring 10 × 5 cm. is a convenient size with which to work. The time occupied in stripping varies with the thickness of the tin layer; 0·0001 inch thickness of unalloyed tin requires approximately 50 seconds; the alloy layer on ordinary tinplate requires approximately 45 seconds. With hot-dipped coatings, the correction given above applies to ordinary commercial coatings having a tin-iron alloy layer corresponding with 3 ounces of tin per base box; a greater correction is necessary for coatings having a higher alloy-content, as referred to later.

INVESTIGATION OF METHOD.—Investigation was carried out to establish the method and to determine its accuracy and reliability.

(i) *Electro-deposited Coatings.*—Pieces of sheet steel (C, 0·08; Si, 0·01; Mn, 0·40; S, 0·035; P, 0·025), 10 × 5 × 0·04 cm., having tin coatings of thickness ranging from 0·0001 to 0·0005 inch deposited from a sodium stannate solution, were tested by the method described. The weight of steel base was found to have decreased, as a result, by 0·002 to 0·003 grm., an amount which would introduce an error of only about 1×10^{-6} inch (0·3 ounce per base box) in the thickness calculated from loss in weight. After the stripping process no tin could be detected on the specimens by a method sensitive to 0·0005 grm.[4]; a very thin film of antimony, weighing 0·0008 grm. on 100 sq.cm., was, however, found by the iodide colorimetric method.[5]

During the period of immersion hydrogen was steadily evolved, accompanied by the separation of spongy antimony, for a time which was roughly proportional to the thickness of the deposit, and varied from 40 to 60 seconds for 0·0001 inch of thickness with specimens initially completely coated. As in the case of the cadmium coatings previously studied,[2] the time of gas evolution for a unit thickness of deposit was somewhat lower when one-half of the specimen was originally not tinned. The cessation of the evolution of gas was abrupt, ranging over about 5 seconds from the period of steady evolution.

(ii) *Hot-dipped Coatings.*—Two grades of commercial tinplate sheet, nominally 1½ and 3½ lb. of tin per base box, were employed. Since some variation in thickness of the tin coating on different areas was anticipated, strips were cut along the length of the sheets (excluding the edges), and these strips were further cut into numbered pieces, giving test specimens measuring 10 × 5 cm. The tin coating on alternate specimens was determined by chemical analysis, and the intermediate specimens were tested by the stripping method. Both methods revealed an increase of 4 to 6 ounces per base box in the tin coating from one end to the other of the sheets. The results obtained by the stripping method, without the application of any correction, were uniformly slightly higher than those obtained by chemical analysis, the average differences of closely agreeing results amounting to 1·09 and 1·04 ounce per base box for the 1½ and 3½ lb. grades, respectively.

In the course of stripping in the hydrochloric acid and antimony chloride solution, the rate of hydrogen evolution remained fairly uniform for a time which was approximately proportional to the thickness of the unalloyed tin layer, as found with electro-deposited coatings; the evolution of gas then slowed down considerably for about 45 seconds before ceasing, and this slow period appeared to correspond with attack of the alloy layer. The period of gas evolution was not sufficiently definite to afford a satisfactory indication of the thickness of coating.

Effect on the tin-iron alloy layer.—Specimens, after stripping and removal of the loose black deposit by swabbing, were smooth, and showed more or less faint dark striations, which followed in outline the pronounced markings of the alloy layer, as revealed after the removal of unalloyed tin from tinplate by the plumbite stripping method.[6] Chemical analysis showed that the amount of tin in the alloy layer was 3·2 ounces per base box for both grades of tinplate tested, and that the amount of tin remaining after stripping in the hydrochloric acid and antimony chloride solution was 0·3 ounce per base box. The bulk of the tin-iron alloy had, therefore, been dissolved, whilst a very thin layer of an alloy present at the iron surface remained unattacked.

Further tests on the alloy layer were carried out on weighed steel pieces coated with known amounts of tin by electro-deposition and subsequently heated under uniform conditions, which had the effect of producing, beneath the tin coating, an alloy layer found to contain 0·038 grm. of tin per 100 sq.cm. (5·5 ounce per base box) without loss of any of the tin coating. On stripping these specimens in the hydrochloric acid and antimony chloride solution, practically the whole of this alloy layer dissolved off, only 0·003 grm. of tin per 100 sq.cm. (0·38 ounce per base box) remaining, as found by chemical analysis. After making allowance for this remaining tin and also for the normal degree of attack on the basis steel in the stripping process as given above, the loss in weight of the steel base showed that 0·0117 grm. of iron, which was previously combined in the alloy, had simultaneously dissolved. This weight of iron is slightly greater than that required by the formula $FeSn_2$ (0·0088 grm.), suggesting that, possibly, an alloy richer in iron was present.

The above results showed that, on stripping a hot-dipped tin coating in the hydrochloric acid and antimony chloride solution, the tin and the iron in the alloy layer are almost completely dissolved, and an empirical correction for the iron, amounting to one-third of the alloyed tin, is necessary. With ordinary commercial tinplate, the alloyed tin appears to be fairly constant within narrow limits at about 3 oz. per base box,[6] for which a correction of 1 oz. per base box, as found in the present work, is appropriate.

(iii) *Effect of the Stripping Solution on Ferrous Basis Metals.*—Mild steel (C, 0·08), high carbon steel (C, 0·82), phosphoric grey cast iron, stainless steel and austenitic nickel-chromium steel were tested by immersion in the stripping solution for 5 minutes. With the exception of cast iron, all the materials remained unchanged in appearance, and the weight loss was less than 0·002 grm. for 10 sq. inch of surface exposed. Cast iron was slowly attacked, with evolution of hydrogen, losing 0·008 grm. for 10 sq. inch of surface.

(iv) *Stripping a Selected Area of Tinplate.*—A single coating of Necol varnish, applied locally with a brush and allowed to dry at room temperature for 15 minutes before immersion, showed no tendency to become detached during the stripping operation. It did not appear essential for the coating to be quite dry to the touch before proceeding with the stripping process. The weight of tin coating on sheet steel found by stripping each face separately was in good agreement with the known total weight. Areas of exposed steel on a partially tinned surface do not require varnishing.

SUMMARY.—A method is described in which the thickness or weight per unit area of tin coatings on steel may be determined by loss in weight of a specimen on stripping the coating in a solution of antimony chloride in hydrochloric acid. The coating dissolves rapidly, a thickness of 0·0001 inch of tin requiring about 1 minute, and the attack on the basis steel is negligible. The method is applicable to both electro-deposited and hot-dipped tin coatings. With hot-dipped coatings, the underlying layer of tin-iron alloy is almost completely dissolved, and a correction for the iron constituent amounting to one-third of the alloyed tin is necessary. Since the alloyed tin on commercial tinplate appears approximately constant at 3 ounce per base box ($1{\cdot}1 \times 10^{-5}$ inch), the correction to be deducted is 1 ounce per base box (4×10^{-6} inch). The tin coating may be protected from the action of the stripping solution by a coating of Necol varnish, thus permitting the determination of thickness on a selected area.

The author is indebted to Mr. J. C. Prytherch, B.Sc., for carrying out some further confirmatory tests.

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The Micro-Determination of the Molecular Weight of Volatile Liquid Compounds

BY A. F. COLSON, B.Sc., A.I.C.

(*Read at the Meeting of the North of England Section, April* 14, 1934)

THE microscopical method originally devised by Barger,[1] and more recently modified by Rast,[2] is probably the earliest method of determining molecular weight on only a few mgrms. of solute. No liquid solutes of low boiling-point were examined by Barger, and it appears from an examination of the original paper that the method is not suitable for such liquids.

Various forms of apparatus have been described[3–6] for the micro-determination of molecular weight by ebullioscopic methods, but no simple micro-apparatus appears to be available for the ebullioscopic determination of the molecular weight of volatile liquids in particular.

The simple cryoscopic method of Rast[2], in which the substance is dissolved in camphor, presents difficulties when applied to the particular case of volatile liquids, on account of the possible loss of liquid by evaporation. Vapour-density methods appear to be superior to all others for the examination of volatile substances.

Two micro-methods for the determination of vapour-density have been described by Bratton and Lochte,[7] and by Niederl and Saschek,[8] respectively. The micro-vapour density apparatus here described gives reasonably accurate results, and is less complicated than those referred to above.

The apparatus is a modification of the macro-form devised by P. Blackmann, and described by him in a number of papers.[9] It consists essentially of a stoppered glass vessel *A* (Fig. 1), a fine bore capillary tube *B* (sealed at one end and containing a short thread of mercury) (Fig. 2), and a small stoppered weighing bottle *C* (Fig. 3).

Before using the apparatus it is necessary to determine the capacity of the vessel *A* when it contains the tube *B* and the bottle *C* (unstoppered). This is done by weighing: (i) when filled with air; (ii) when completely filled with distilled water. The capillary tube *B* is most conveniently prepared in the following manner:

A piece of thermometer stem is very thoroughly cleaned and dried. One end of the tube is sealed in the Bunsen flame, and the open end is immediately dipped into a little pure dry mercury; when the mercury has risen in the capillary tube to a height of about 0·6 cm. the tube is withdrawn and allowed to cool to room temperature.

The determination of molecular weight is carried out in the following manner: —The capillary tube *B* is clamped in a vertical position, and the length (L) of the air-thread enclosed by the mercury is measured by reading the divisions marked on the tube. The temperature (t_1) is recorded at the same time.

The capillary is now introduced into the vessel *A*, together with the weighed liquid contained in the stoppered bottle (*C*). The apparatus is set in a vertical position, and the stopper *D* is brought into position by means of the thread attached to it.

The length (L_c) of the air-thread is now measured as before. If the stopper (*D*) has been manipulated with sufficient care, the value (*L*) does not usually differ from L_c.

It is absolutely essential that the closed apparatus shall be air-tight during the next stage of the determination. The joint between the stopper *D* and the edge of the neck of the vessel *A* is therefore covered with a small amount of a concentrated solution of celluloid in amyl acetate.

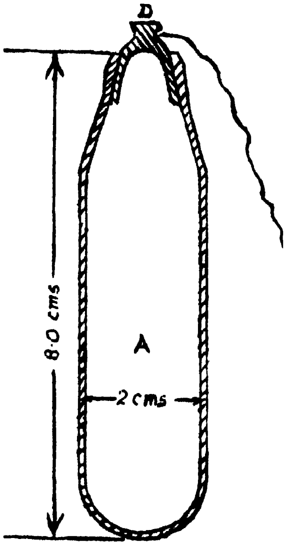

Fig. 1.

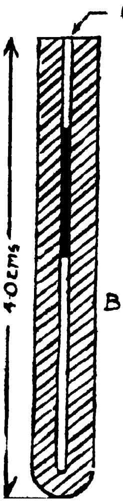

Fig. 2.

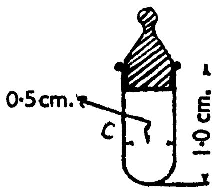

Fig 3.

When this solution has evaporated to dryness, the apparatus is heated in a suitable oven to a temperature (t_2) about 40° C. above the b.pt. of the particular liquid under examination, and the length (*k*) of the air-thread is measured at short intervals during a period of about 5 minutes. The minimum value is recorded as the correct length.

The vapour-density is calculated from the formula

$$d = \frac{31068 wkL_c (273 + t_1)}{PLV (L_c - k)}$$

where *d* represents the density relative to hydrogen; *V*, the volume of vessel *A* determined as already described; *w*, the weight of substance taken in grms.; and *P*, the atmospheric pressure in mm. of mercury. The molecular weight is obtained by multiplying the value of "*d*" by two.

The derivation of the formula is given by Blackmann in the references at the end of this paper.

The following table contains some of the results obtained for the molecular weight of acetone. ($d = 29{\cdot}0$.) (Mol. weight = 58·0.)

V Ml.	P Mm.	t_1 °C.	W Mgrm.	L Divs.	L_c Divs.	k Divs.	d
13·93	768·8	22·5	8·84	12	12	9·5	28·8
,,	,,	21·0	7·14	,,	,,	9·8	27·12
		23·0	13·10			8·8	30·90
		23·0	9·15			9·3	27·10
		23·5	10·40			9·1	28·10
		23·5	8·80			9·6	30·30

I wish to express my thanks to the Directors of Imperial Chemical Industries, Ltd., for permission to publish this work, which was carried out in the Research Laboratory of their subsidiary Company, Imperial Chemical Industries (Alkali), Ltd., Northwich.

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Notes

The Editor wishes to point out that the pages of the Journal are open for the inclusion of short notes dealing with analytical practice and kindred matters. Such notes are submitted to the Publication Committee in the usual manner.

THE APPLICATION OF FILTERED ULTRA-VIOLET RAYS IN THE INVESTIGATION OF POISONING CASES

VARIOUS Continental workers[1] have carried out researches on the use of filtered ultra-violet light in the medico-legal detection of poisons.

Among these, Danckwortt and Pfau[2] express the opinion that inorganic substances, and certain alkaloids, especially morphine, lend themselves to detection by filtered ultra-violet light.

Examination of inorganic substances is carried out by direct exposure, while with solutions Goppelsroeder's method of capillary analysis, as modified by Ernst and Jentschitsch,[3] is used.

In the writer's experience the only fluorescent substance of medico-legal importance in the inorganic group is calomel, which, when exposed to the rays, exhibits a brilliant salmon-pink luminescence. As regards alkaloids in solution the fluorescence shown is in no way specific or characteristic.

Since many different substances give the same colour zones, no useful purpose is served by the employment of filtered ultra-violet light, more particularly when the range of delicate analytical tests at present available permits of accurate results. Furthermore, the presence of impurities, by giving rise to adventitious fluorescence, may completely mask any results obtained.

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THE DETERMINATION OF TARTARIC ACID IN CIDER

To 100 ml. of cider, containing about 5 per cent. of alcohol (by vol.), are added 2 ml. of glacial acetic acid, 0·5 ml. of potassium acetate solution (20 per cent.), and 15 grms. of pure potassium chloride in the form of powder. When solution is complete, 15 ml. of 95 per cent. (by vol.) alcohol are added, the mixture is stirred thoroughly, and the beaker is covered and allowed to stand overnight. Its contents are then filtered through a Gooch crucible charged with paper pulp, and the residue is washed three times with 20 ml., in all, of wash liquor (15 grms. potassium chloride in 100 ml. of water, and 20 ml. of 95 per cent. alcohol). The pulp and precipitate are returned to the beaker by means of hot water, and the liquid is titrated at boiling-point with 0·1 *N* sodium hydroxide solution (phenolphthalein as indicator). Each 1 ml. of alkali ≡ 0·015 grm. of tartaric acid.

This method, which is substantially the German 1921 wine method, has met with considerable criticism. With a few slight modifications, however, it may be made a useful routine test for cider.

(i) A solubility correction must be added to the titration figure. This is usually given as 1·5 ml. of 0·1 *N* sodium hydroxide solution, but I find it to vary from 0·7 ml. at 15° C., to 1·15 ml. at 20° C. and to 1·6 ml., at 25° C. These are averages.

(ii) National mark ciders may not contain more than 1 grm. per litre of tartaric acid. Here precipitation of potassium hydrogen tartrate may be very slow and incomplete. Hence, 0·2 grm. of pure potassium hydrogen tartrate should be added before the alcohol, and subtraction from the titration figure must be made, besides addition of the solubility correction. Examples:

	A Per Cent.	B Per Cent.
With potassium hydrogen tartrate	0·057	0·065
Without potassium hydrogen tartrate	0·024	0·025

(iii) Ciders may contain from 2 to 3 grms. per litre of tartaric acid. The potassium hydrogen tartrate will begin to settle out even before the alcohol is added. The 0·5 ml. of potassium acetate is inadequate, but 2 ml. have been found sufficient in all cases examined. Thus:

C

	Potassium acetate solution	Tartaric acid Per Cent.
	0·5 ml.	0·292
	1·5 ml.	0·312
	3 ml.	0·309
(Saponified)	2 ml.	0·318

D

	Potassium acetate solution	Tartaric acid Per Cent.
	2 ml.	0·312
	3 ml.	0·308
(Saponified)	2 ml.	0·321

(iv) **Variations in alcohol-content of the cider.**

Alcohol Per cent. (by vol.)	Solubility corr. at 20° C. Ml. of 0·1 *N* NaOH
0	1·35
5	1·05
10	0·9
15	0·8

The error due to this cause is insignificant. These conclusions are exemplified by the following determinations of tartaric acid in two ciders:

	Potassium acetate Ml.	Potassium hydrogen tartrate Grm.	Tartaric acid Grm.	Sodium hydroxide solution Ml.	Tartaric acid found Per Cent.
5 per cent. alcohol	0·5	0·2	—	9·5	(corr. 1·1 at 18·5°C.)
Cider E	0·5	0·2	—	13·7	0·063
,, ...	2	—	0·2	16·2	0·260
,, F	0·5	0·2	—	15·05	0·083
,, ...	2	—	0·2	17·7	0·282
Standardisation ..		0·2		10·6	

(v) *Influence of colloids.*—Whilst malic, lactic and citric acids, tannin, sugar and potassium phosphate do not interfere with the accuracy of this test, additions of pectin in the proportions present in cider cause the results to be low.

Pectin, per cent.	0	0·05	0·1	0·2	0·3
Tartaric acid found	0·197	0·190	0·187	0·186	0·185

When weighed quantities of tartaric acid are added to cider the results are generally slightly low. The deficiency is independent of the amount of tartaric acid present, and from the average of my tests amounts to 0·0075 grm. Some allowance for this can be made by increasing the solubility allowance by 0·5 ml.

Tartaric acid, freshly added to cider, can be fairly accurately accounted for, but not when it has been added for some time. Bacterial destruction takes place, perhaps esterification occurs, and precipitation of potassium hydrogen tartrate, and calcium tartrate has been encountered.

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Messrs. Gaymer & Co., Attleborough

A NEW CONSTANT FOR FIXED OILS—HYPOCHLOROUS ACID VALUE

The substitution which occurs in the ordinary methods of determining the degree of unsaturation of an oil is to a large extent eliminated by using hypochlorous acid as the reagent. The method consists in saponifying the oil neutralising the solution (bromthymol blue as indicator), and then determining the amount of hypochlorous acid absorbed by the sodium salts of the fatty acids. It is not necessary to remove completely the alcohol used in the saponification.

Five ml. of sodium hypochlorite solution (prepared from bleaching powder solution and sodium carbonate, containing slight excess of sodium carbonate and brought approximately to the strength, 5 ml. ≡ 20 to 25 ml. of *N*/10 thiosulphate solution) and excess of potassium iodide solution are put into a conical flask and acidified with sulphuric acid (dil.). The liberated iodine is titrated with thiosulphate solution, and the test is repeated with standard sulphuric acid solution; the volume of the latter required just to liberate the full amount of iodine from the solution is thus determined. From the reactions—

$$(a)\quad \mathrm{Na_2CO_3 + H_2SO_4 = Na_2SO_4 + H_2O + CO_2}$$

$$(b)\quad \mathrm{2NaOCl + H_2SO_4 = Na_2SO_4 + 2HOCl}$$

$$(c)\quad \mathrm{2HOCl + 4KI = 2KOH + 2KCl + 2I_2}$$

$$(d)\quad \mathrm{2KOH + H_2SO_4 = K_2SO_4 + 2H_2O}$$

the amounts of sulphuric acid required, respectively, to neutralise the sodium carbonate of the hypochlorite solution, to liberate hypochlorous acid and to neutralise the potassium hydroxide in equation (*c*) are determined. From 0·12 to 0·125 grm. of oil is saponified in the usual way with 25 ml. of approx. *N*/5 alcoholic potassium hydroxide solution. The excess of the alkali is exactly neutralised with standard hydrochloric acid, bromothymol blue being used as indicator, and the alcohol is then evaporated on the water-bath until a pasty mass remains. The soap is dissolved in water, and the solution is transferred to a 750-ml. flask and diluted to 600 ml. To this 5 to 8 ml. of sodium hypochlorite solution are added, followed by just enough sulphuric acid of known strength to neutralise the free sodium carbonate and to liberate hypochlorous acid from the hypochlorite. The flask is quickly closed by means of a rubber stopper fitted with a dropping funnel containing potassium iodide solution, well shaken, and kept in a dark and cool place for 5 to 15 minutes. The potassium iodide solution in the funnel is then blown in and the flask well shaken, after which the dropping funnel is washed and taken out. The solution is now acidified with excess of dilute sulphuric acid, and the liberated iodine is titrated with standard thiosulphate solution. A blank test is made at the same time, and the difference between the thiosulphate figures gives the amount of hypochlorous acid absorbed (1 ml. N/10 thiosulphate ≡ 0·002625 grm. of HOCl).

The following results are typical of those obtained:

Oil or fat	Iodine value	=	HOCl value	Time of absorption	Hypochlorous acid absorbed Per Cent.
Arachis	87·6		18·1	15 minutes	18·0
Buffalo ghee	35·4		7·3	do.	7·8
Coconut	9		1·9	do.	1·9
Olive	88		18·2	do.	17·6
Mustard	108		22·3	do.	22·3
Sesame	110		22·7	do.	22·1
	—		—	1 hour	22·6
Linseed	185		38·2	15 minutes	35·1
				2 hours	35·3
Fish (*Clupea ilisha*)	88		18·2	15 minutes	17·8

The results obtained in these and analogous experiments have shown that the absorption is complete in 5 to 15 minutes, and that the time factor has no material influence.

We wish to express to Dr. H. K. Sen our thanks for his advice throughout the work.

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NOTE ON THE EXAMINATION OF DRIED GREEN MINT

VERY considerable quantities of mint (*Mentha viridis*, Linn.) are grown for culinary use, apart from the crops raised for distillation of the essential oil.

Although the herb has no food value, it is consumed, in the aggregate, in quite notable amounts, and although a few shipments from abroad have been found adulterated with other leaves, it is not usual for a herb, which grows near the soil and needs careful cultivation to keep it clear of weeds, to be found mixed with the leaves of a tree growing to a considerable height.

The identification of adulterants is not a difficult matter for anyone with a knowledge of plant histology, but there are other factors which determine the quality of mint, and of these the following are of significance:—(i) Absence of an undue proportion of stem; (ii) freedom from old brown leaf; (iii) absence of earthy impurity and sand; (iv) presence of a due proportion of volatile oil.

ANALYSES OF DRIED MINT

Total ash Per Cent.	Alkalinity of water-soluble ash, as K_2O Per Cent.	Ash insoluble in hydrochloric acid Per Cent.	Volatile oil by volume Per Cent.
12·15	1·94	1·84	1·1
10·78	1·02	0·63	
11·75	1·87	0·99	1·4
11·03	1·58	0·65	
10·95	1·97	1·10	
10·43	1·35	1·20	
9·7	1·44	0·85	1·41 (English)
10·76	1·21	1·2	
11·31	1·61	0·82	0·92 (French)
9·81	1·23	0·82	
10·29	1·42	0·78	0·84
10·78	2·37	10 per cent. stalk	
12·15	2·04	8 per cent. stalk	
10·39	2·35	— (Belgian)	
9·37	1·67	0·43 (*Ailanthus* present).	

The herb grown in this country is sold, in season, in the fresh green state, but for out-of-season requirements it is dried and rubbed through sieves. If the herb is cut before it has attained the flowering stage the bulk of the stem is too large to pass through a number 10 sieve, and, consequently, the requirement that dried rubbed mint shall contain not more than 2 per cent. of stems above 3 mm. in diameter, is a reasonable one, but it does not prevent the inclusion of a quantity of almost wire-like small stems if the crop had been left too late before harvesting.

The presence of brown leaf means diminished flavouring qualities.

Earthy impurities, and more particularly sand, should be strictly limited. The presence of both is usually indicative of harvesting in wet weather, which splashes soil on to the leaves, and some limit ought to be recognised for such impurities. The "ash" is a good indication of the cleanliness of the sifted herb, and the amounts which are soluble in water and the proportion insoluble in hydrochloric acid are a useful guide to quality and genuineness.

The amount of essential oil in the fresh herb is variable, and the process of drying introduces an unknown loss, but the flavour of a well-dried "mint" depends on the proportion of oil it contains.

The analyses of a number of typical samples, representing many hundreds of bales, have afforded me the following figures, which should be some guide to the quality of the supplies marketed. The greater number were of foreign origin, but it is hoped to increase the home-grown crop, and, if possible, to improve the flavour by more satisfactory methods of drying.

The examination of the mint for arsenic showed its presence in a few samples in proportions up to one-thirtieth of one grain per pound. This may be attributable to the contamination with earthy matter which contained it, or possibly to the use of arsenical sprays in the vicinity of the growing herb.

C. EDWARD SAGE

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LOSSES IN MEAT ON COOKING

WE have read with great interest, and not a little astonishment, the note on the above subject on page 405 of the June issue of the ANALYST. This Laboratory has been associated with the investigation of chilled beef and frozen beef from the Argentine and Australia for over forty years—in fact, since the early days of commercial shipments of chilled meat from the Argentine. We have done numerous cooking experiments, but we have never obtained such divergent results between the losses on cooking of fresh English beef and chilled beef. With frozen beef one would expect much greater losses, owing to exudation of the contents of the broken cells—a phenomenon which can readily be observed under the microscope. In the case of chilled beef, stored during transit at temperatures round about 30° F., the cells are not broken or burst, and there would appear to be no reason why such chilled beef should show excessive loss of weight on cooking.

We understand that Mr. Arnaud's results have been based upon cooking pieces of steak of about 1 lb. weight. In our own experiments, carried out recently, we were unable to confirm his results upon such small samples, and we also extended the experiments to include joints of various sizes.

In order to place the reliability of the samples beyond question, Lt.-Colonel Dunlop Young, O.B.E., the lately retired Chief Meat Inspector at Smithfield, kindly consented to purchase the meat in the ordinary way of retail trade from a butcher in the City, and to hand the meat to us.

By courtesy of the Gas Light & Coke Company we were provided with two carefully equalised gas cookers (New World No. 3 with Regulo Control), and on each occasion an English joint was cooked in one oven, and an Argentine chilled joint, of approximately equal weight was cooked in the other. A member of the staff of the Gas Company assisted with the cooking and acted as a neutral observer of the whole of the experiments.

Each joint was carefully weighed just before it was placed in the oven, and weighed again after it had been cooked and had cooled, and the dripping and gravy were each carefully weighed. The digestion experiments were carried out upon 10 grms. of the minced lean, in 100 ml. of distilled water containing 1 ml. of 20 per cent. hydrochloric acid and 0·5 grm. of pepsin. This mixture was placed in an incubator at 37·5° C. for four hours, and was then filtered, after which the undigested fibrin was dried and weighed. The moisture was determined in the original lean meat after cooking, and the undigested fibrin was calculated on the dried lean. The mineral matter was determined by ashing the wet lean in platinum crucibles.

These figures, which have been obtained as the result of unbiassed investigation by three independent workers, show that the loss of weight on cooking English beef and Argentine chilled beef is approximately identical. Moreover, the digestibility, mineral-content and nett loss of weight on cooking are also so nearly identical as to make it quite safe to say that meat of either kind is equally economical, quite apart from price.

LOSS OF WEIGHT ON COOKING ENGLISH JOINTS AND CHILLED ARGENTINE JOINTS AND THE RESPECTIVE DIGESTIBILITY AND MINERAL-CONTENT OF THE COOKED MEATS

Nature of joint	Weight of joint ozs.	Weight of joint after cooking ozs.	Gross loss of weight ozs.	Per-centage loss of weight (gross)	Weight of dripping ozs.	Weight of gravy ozs.	Weight of joint + dripping + gravy ozs.	Nett loss of weight ozs.	Per-centage loss of weight (nett)	Moisture in lean (dried at 105° C.) Per Cent.	Mineral matter in wet lean Per Cent.	Un-digested matter (calc. on dry lean) Per Cent.
Scotch sirloin	78·75	61	17·75	22·5	8·25	0·2	69·45	9·3	11·7	63·25	1·0	20·7
Argentine sirloin ..	78	59	19	24·3	9·25	0·4	68·65	9·36	11·8	67·5	1·1	15·0
English wing end ..	183	126	57	31·1	29·75	1·25	157	26	14·2	58·4	1·0	17·8
Argentine wing end ..	182·25	120	62·25	34·0	32·0	2·0	154	28·25	15·4	59·2	1·05	13·5
Grilled English steak ..	15·5	13·5	2	13·0	—	—	—	2	13·0	65·9	1·00	20·7
Grilled Argentine steak..	17·0	15·0	2	11·7	—	—	—	2	11·7	63·7	1·27	21·6
English top side.. ..	80·0	55·25	24·75	30·9	9·6	1·3	66·25	13·75	17·2	66·1	1·20	16·3
Argentine top side ..	81·5	56·75	24·75	30·3	8·25	1·36	66·06	15·44	19·5	66·6	1·22	11·5
English wing rib ..	161	110	51	31·6	26·68	1·06	137·75	23·25	14·3	61·5	1·02	23·5
Argentine wing rib ..	178	122	56	31·4	29·5	1·19	152·69	25·31	13·4	64·7	0·97	36·0
English fried rump steak	17	14·75	2·25	13·2	—	—	—	2·25	13·2	65·5	1·07	22·1
Argentine fried rump steak	18·75	16·0	2·75	14·4	—	—	—	2·75	14·4	65·8	1·10	19·8
English top side.. ..	80	56·75	23·25	29·4	8·06	1·18	66	14	17·9	67·0	1·20	16·3
Argentine top side ..	80·5	53·5	27	33·7	10·5	0·5	64·5	16	20·0	63·7	1·12	18·2

These results may be summarised as follows:

	Argentine chilled beef Per Cent.	English beef Per Cent.
Average gross loss of weight	25·7	24·5
Average nett loss of weight (taking account of dripping and gravy)	15·1	14·6
Mineral matter in wet lean after cooking	1·12	1·07
Undigestible matter (calculated on dried lean)	19·3	19·6

A. SCIVER

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The results obtained by Mr. Sciver have been submitted to me by the Editor.

The four pieces of meat enumerated in my experiments already published (*loc. cit.*) were supplied to me by a butcher holding a high position in his trade. Each piece of meat was labelled, and I still possess the labels. In answer to an enquiry addressed to him, the butcher concerned replied:—"There can be no question that the piece of steak despatched to you . . . with label attached was chilled Argentine, as described. Unfortunately, I kept no record of any particular brand, but it must have been 'X' or 'Y,' as my purchase book shows.

"You may be sure that I was very particular with regard to the despatch of the samples; in fact, I cut and packed them myself."

A further sample of meat upon which similar experiments were made was supplied by another butcher, and he also assures me that the meat supplied was Argentine chilled.

The results published were obtained on meat cooked and weighed by me both before and after cooking.

F. W. F. ARNAUD

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MAIDSTONE, KENT

Notes from the Reports of Public Analysts

The Editor would be glad to receive the Annual or other Reports of Public Analysts containing matter of special interest to the Society. Notes made from such Reports would be submitted to the Publication Committee.

CITY OF BIRMINGHAM

REPORT OF THE CITY ANALYST FOR THE FIRST QUARTER, 1934

OF the 1481 samples submitted by the Food and Drug Inspectors during the first quarter of the year, 1424 were taken informally. Fifty-four samples were adulterated, and two were incorrectly labelled.

ASPIRIN TABLETS.—One, out of five samples, was of very inferior quality, and contained 2 per cent. of free salicylic acid, corresponding with 2·6 per cent. on the aspirin used; the B.P. limit for salicylic acid is 0·05 per cent., so that over fifty times too much was present. In addition, over 6 per cent. of French chalk was contained in the tablets—an unusually large quantity. Most tablets contain no insoluble mineral matter, and it seems quite unnecessary to incorporate any such material in tablets of this kind. No further action could be taken, as the tablets in question were old stock and the packers had gone out of business.

DRIED MINT.—Two samples were found to be adulterated with about 25 per cent., and 35 per cent., respectively, of *Ailanthus* leaves. There have been, during the last twelve months, a number of prosecutions in this country, both of retail vendors and of wholesale firms, for the sale of such adulterated mint (*cf.* ANALYST, 1934, 535), and it has been shown that the adulteration has been carried out before importation and that a number of reputable wholesale firms have been deceived. The firms concerned with the supply of the two samples mentioned were communicated with, and both have recovered all the adulterated mint supplied to the shops in question and have done everything in their power to collect as much as possible from their retail customers all over the country.

TEA "WITHOUT TANNIN."—One sample was stated on the label to contain all the essential goodness of tea without any injurious tannin. The analysis showed that 13·9 per cent. of tannin was present.

The label on another sample (China tea) described it as practically free from tannin, a quite incorrect statement, since 8·6 per cent.—a normal amount for China tea—was found to be present. Both the firms concerned were cautioned, and agreed to discontinue the use of the incorrect descriptions.

H. H. BAGNALL

CITY OF LEEDS

ANNUAL REPORT OF THE CITY ANALYST FOR 1933

THE total number of samples analysed in 1933 was 3696, of which 1985 were food and drugs, and 69 were fertilisers and feeding stuffs. Of the food and drug samples, 186 were adulterated.

FORM OF MILK CERTIFICATE.—During the hearing of a case the Stipendiary Magistrate asked me if it would not be better to base the percentage of added water on the freezing-point rather than on the non-fatty solids, and on being told that such a course had already been adopted by one County Council who were making use of Section 4(1) of the Milk and Dairies (Amendment) Act, 1922, His Worship said that due consideration might be given to this matter. The outcome of this suggestion has been a re-drafting of the form of certificate, following a consultation with the Town Clerk, who decided, however, not to proceed under the Milk and Dairies (Amendment Act), 1922, which forbids, amongst other things, the addition of water to milk intended for sale, and the sale of any milk to which any such addition has been made, but to make continued use of the Food and Drugs (Adulteration) Act, 1928. In a case where a milk contains less than the 8·5 per cent. of non-fatty solids required by the Sale of Milk Regulations, 1901, and has a freezing-point higher (that is, nearer 0° C.) than —0·530° C., the minimum amount of water added to the milk is now calculated from the freezing-point.

This was done in the successful prosecution of two retailers in partnership, for selling milk containing at least 26 per cent. of added water. The matter was carried a step further when a farmer appeared on February 7th for selling 2 samples of milk which the freezing-point showed to contain at least 3·8 per cent. and 4·2 per cent. of added water, respectively.* Before use was made of the freezing-point, it was the practice to prosecute only in respect of milks containing a minimum of 5 per cent. of added water (even though satisfactory appeal-to-cow samples had been obtained within 48 hours) in order to allow for the remote possibility of an appreciable day-to-day variation in the composition of the milk.

SAGO.—All 4 samples submitted proved to be tapioca. As a result, a letter was sent by the Medical Officer of Health to the Leeds and District Grocers and Provision Dealers Association, and this letter was read at a meeting of the latter on February 28th, 1934, following which some prominence was given to the matter in the local press, and since then one firm has displayed in its window the various forms of tapioca on sale. These are Flake, Seed Pearl, Medium, and Bullet. Sago is usually of the same size as pearl tapioca, but is brown.

BISMUTHATED MAGNESIA TABLETS.—One sample was bought and found to be 6·8 per cent. deficient in the amount of bismuth carbonate declared, and 34·2 per cent. deficient in magnesium carbonate. There was also present 9·3 per cent. of talc, which was undeclared on the label. The retailers were communicated with respecting these matters.

C. H. MANLEY

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* The first sample contained 3·15 per cent. of fat and 8·10 per cent. of solids-not-fat, and the second 3·70 per cent. of fat and 7·90 per cent. of solids-not-fats. The figures for Δ were 510 and 508, respectively. An appeal-to-cow sample gave: fat, 3·70; solids-not-fats, 8·70 per cent.; Δ, 547.—C. H. M.

Department of Scientific and Industrial Research

FUEL RESEARCH

ANALYSIS OF COMMERCIAL GRADES OF COAL. PART II*

THIS report marks the completion of a systematic examination of the commercial grades of coal produced and marketed in the South Yorkshire, Nottinghamshire and Derbyshire coalfield. It deals with the output of 17 collieries producing 130 grades of coal, which range from those yielding good metallurgical coke to non-coking coals. They include the well-known Yorkshire "hards," first-class locomotive fuel, as well as general steam-raising, gas and household coal.

The sampling was carried out at the pit-head—at the conveyor belts or at chutes delivering the coal to wagons or store. The period of sampling and the number and size of the increments were decided after a consideration of the hourly fluctuations of the coal. The gross samples were taken by hand, but the reduction to laboratory size was carried out in a mechanical crushing and sampling equipment mounted on a commercial motor van and operated from the engine by auxiliary shaft and driving gear.

The work done on these samples and the presentation of the results follow exactly the lines of a previous report (Survey Paper No. 20) dealing with 39 collieries in the same area. Each colliery is dealt with separately, the grades of coal samples from it are listed, and the sizes are given. For each grade is given a proximate analysis, the contents of sulphur, nitrogen and chloride, and the calorific value. In addition, the percentage of phosphorus is given for grades that are suitable for coke manufacture, and, in certain cases, the results of ultimate analyses and of laboratory carbonisation assays at 600° C.

The sampling of commercial grades of coal at the pit-head is a natural corollary to the examination of the seams as they occur below ground, which is being undertaken under the Fuel Research Board in the Physical and Chemical Survey of our National Coal Resources. A study of the seams shows us the material as it is or might be mined or marketed, where to look for this or that quality, how best to conserve our supplies of those coals suited for special purposes, and how to develop workings to best advantage. Commercial sampling shows us the material as it is actually handed over to the consumer, sometimes as the carefully prepared product of a single seam, sometimes as a blend of several seams.

In the South Yorkshire area the Parkgate, Barnsley and Silkstone, three of the chief seams, have already been examined as they occur in the field, and this part of the work is continuing. In most cases in the present report one or more of these seams forms part of the commercial output examined, and it is interesting to note the close agreement between the results obtained and those given by samples of the seams cut underground.

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* Fuel Research Survey Paper No. 31. Yorkshire, Nottinghamshire and Derbyshire Coalfield. Part II. H.M. Stationery Office, 1934. Price 9d. net.

Government of Madras

ANNUAL REPORT OF THE CHEMICAL EXAMINER FOR THE YEAR 1933

IN his Annual Report Lt.-Col. Clive Newcomb states that the work of the department shows a marked increase over the preceding year (1518 cases with 7129 articles, as against 1437 cases with 6136 articles in 1932). The rise is due entirely to the amount of medico-legal work, the general analyses having diminished from 198 articles in 1932 to 170 in 1933. It is probable that the increase is due to greater care in the investigation of crime rather than to an increase in crime.

HUMAN POISONING CASES.—During the year there were 372 cases, with 2116 articles, in which 450 persons were affected and 277 died. Poison was found in 173 cases, opium heading the list with 28 cases, and oleander coming next with 27 cases. Arsenic was found in 22 cases, and mercury in 17, and there were three cases of poisoning by datura or other mydriatic alkaloidal poison.

Dried Snake Venom as Poison.—In a case of attempted suicide to avoid a charge of murder, a man was admitted to the hospital semi-conscious and in a state of collapse. It was stated that he had injected into himself some poison through a small wound on the left thigh. White arsenic (9/10 grain) was found in the viscera. One of the articles received in this case was a packet containing yellowish translucent scales. The powder had the usual appearance and chemical properties of dried snake venom, and was definitely proved to be snake venom, by its fatal effects when injected into a guinea pig, and by the absence of fatal effects when injected along with anti-venin serum. The man had therefore probably taken arsenic by the mouth, and, as an additional precaution, injected snake venom into the wound in his thigh, in a resolute attempt to commit suicide.

Arsenic in Love Potions.—Love potions are not unusual articles to be sent for examination and frequently contain dangerous poisons. One examined this year contained 3½ grains of white arsenic—a dose which would very likely prove fatal. It would be questionable if these so-called love potions are not sometimes given on account of love for some person other than the recipient. Where a wife has given poison to a husband it forms a useful defence, if need be, to aver that the poison was given as a love potion, as in the following case.

Barium Poisoning.—A man was given some powder in soup by his wife and subsequently developed symptoms of acute gastro-intestinal irritation. The next day, although vomiting had ceased, he had severe pain in the abdomen and numbness and pains in his limbs. Gradually his speech became incoherent, and he became unconscious and died on the third day. The powder said to have been given was found to be a mixture of barium carbonate and barium sulphide, and the viscera were all found to contain barium. In some of the bed linen soiled by excretions we were unable to find any barium. The wife was acquitted chiefly on two grounds: (1) the judge held that proof of poisoning by barium was incomplete, in that the doctor who did the post-mortem had not stated that the rectum was congested, and this is said in some books to be a sign to be found in fatal cases of barium poisoning, and in that we had not found barium on the bed linen; and (ii) the woman gave a defence that she had only given the powder as a love potion.

Copper Sulphate Poisoning.—Although copper sulphate is not a very deadly poison on account of the violent vomiting it produces, it sometimes happens that, owing to collapse, vomiting is insufficient to eliminate the poison, and the victim dies. In one such case copper was found in all the viscera analysed, and the amounts found are of interest, as this is not a very common form of fatal poisoning.

A woman died suddenly. The stomach contained some bluish-white material, and the lungs, liver and kidneys were all congested. The stomach contained copper equivalent to about 32 grains of crystalline copper sulphate, and the stomach-contents contained about 10⅓ grains. In the small intestines the amount of copper was equivalent to about 18 grains of the sulphate, in the liver it was equivalent to about 2/5 grain, and in one kidney the amount was equivalent to about 3/5 grain.

Madar Juice Poisoning.—From time to time cases of fatal poisoning from drinking the milky juice of the plant *Calotropis gigantea* are investigated in the laboratory. The symptoms of madar juice poisoning are not very clear, as in most cases little information is available as to their nature. It would appear to be not only a gastro-intestinal irritant, but also a cerebro-spinal poison.

In one case a woman drank the juice at about 7 a.m. The symptoms began at 7.30 with vomitings and purgings followed by convulsions in which she rolled on the ground. She collapsed and died at about 8 a.m. The post-mortem signs were bloody discharges in the nostrils and mouth, the lungs were congested, and the heart was empty. Trachea was injected, liver, spleen and kidney were congested. The stomach was congested and contained about 2 oz. of chyme-like fluid. The small intestines were congested, the brain and the membrane were also congested. The reactions of madar juice were given by the stomach and its contents in this case.

In another case of post-mortem there was no discharge from the nose and mouth. The lungs were congested, the pericardium was congested, the heart was empty and congested and there was congestion of the trachea, of the stomach, liver, spleen, small intestines and brain. A four-months-old foetus was found in the uterus. The reactions of madar juice were obtained from the stomach and contents in this case.

In addition to being taken by the mouth, madar juice is often used as an abortifacient, and, when so used, is inserted into the uterus on a small tampon.

Further investigation of the composition of madar juice has been made. One hundred ml. of the juice yielded 15·12 grms. of total solids, and 1·75 grm. of ash. The crystalline extract obtained from an alcoholic extract of the juice after saponification and extraction with ether (ANALYST, 1934, 37) has been examined. After repeated crystallisation it yielded a white crystalline substance containing: Carbon, 80·5; hydrogen, 11·53, and oxygen, 7·93 per cent., corresponding with the formula, $C_{27}H_{46}O_2$; mol. weight (average of several determinations) 405; iodine value (pyridine sulphate dibromide method), 63·2.

In routine analysis of articles for madar juice the following system of examination can be used:—To the alcoholic extract of the suspected substance alcoholic potash is added until the liquid is alkaline, and the whole is heated on a water-bath to drive off the alcohol. The residue is taken up with water and extracted with ether. The ethereal extract is tested as mentioned in the last annual report (*loc. cit.*). Presence of madar is further confirmed by distilling the above-mentioned aqueous residue after extraction with ether, with alcohol and 50 per cent. sulphuric acid. The characteristic smell of madar esters may be recognised in the distillate.

Poisoning with Marking Nut.—A man was accused of pouring some blistering liquid on to a woman, and stained portions of cloth were sent for examination. The stains were extracted with alcohol, the alcoholic extract was treated with lead acetate to precipitate proteins and organic acid and filtered, lead was removed from the filtrate by means of ammonium oxalate, and the filtrate from the lead precipitate was diluted with water and extracted with petroleum spirit. The extract, when evaporated, left a thick brownish liquid, becoming bluish-green on addition of potassium hydroxyde (a chemical reaction of marking nut). A little of the liquid, when rubbed on the skin of the hand, produced, after two days, very severe irritation and blistering, the blisters tending to spread along the margin until the whole of the back of the hand was swollen and blistered. There was intense itching and oozing of serum, and the back of the hand was stained black for some weeks where the juice had been applied. The delayed action of marking nut juice or of the extract from it is very striking, and makes it a very dangerous poison (*cf.* ANALYST, 1932, 57, 796).

Areca Nut Poisoning.—The investigation on areca nuts has been continued, with a view to throwing some light on cases of poisoning by areca nut occasionally reported. Air-dried areca nuts contained 11·0 per cent. of moisture, and yielded 11 per cent. of fat on extraction with ether. The fat melted at 49° C., had n_D^{51}, 1·450, saponification value, 203, and iodine value, 26·5. It had no toxic action on frogs. The nuts yielded 0·8 per cent. of ash. The alkaloids are difficult to extract, as they are only sparingly soluble in the common organic solvents, and the difficulty is enhanced by the fact that the small portion of the alkaloidal fraction extractable with ether volatilises at the temperature of the steam-oven. A few mgrms. of an alkaloidal fraction were obtained by extraction of an ammoniacal aqueous extract of the defatted sample with ether, followed by spontaneous evaporation of the ether. The residue gave precipitates with phosphotungstic acid and Mayer's reagent. A portion injected into a frog produced paralytic symptoms, but the frog ultimately recovered. The investigation is still in progress (*cf.* ANALYST, 1932, 57, 391).

EXAMINATION OF BOMBS.—Forty-two cases (with 236 articles) in which bombs were concerned were investigated, and there were also 7 cases (with 24 articles) in which explosives other than explosives legitimately imported had been used.

Most of the exhibits were bombs or the remnants from the explosion of bombs of the kind usual in South India, *viz.* with a mixture of potassium chlorate and arsenic sulphide as the explosive agent. Such a mixture is safe to handle when wet, but, when dry, explodes very violently on percussion or friction. Experiments showed that the mixture was safe to handle while wet with alcohol, but after evaporation of the alcohol the experimental bomb exploded very violently when thrown on to a hard gravel path.

In a series of connected cases bombs of a different type were used. In these, gunpowder formed the explosive, and was set off by the action of sulphuric acid on a mixture of sugar and potassium chlorate. A brass vessel with a screw top, known as a *kooja*, was used as the container, and the whole bomb was a very dangerous affair, perhaps more dangerous to the man who was throwing it than to the persons at whom it was thrown, since the setting-off arrangements were very primitive, and the bombs were liable to go off (and *two* of them did) when they were not intended to do so.

Among the articles captured by the police in these cases were various materials for making these bombs. In addition to ordinary gunpowder, there was a mixture of potassium chlorate and nitrate as the oxidising agent, and dried coffee grounds instead of charcoal. Although not so good as a properly-made gunpowder, this mixture was quite a powerful explosive when set off in a confined space.

The danger of allowing the usual chlorate and arsenic sulphide mixture to dry was shown by an explosion of some exhibits which were being sent back to the local court after having been shown in the appeal court.

IDENTIFICATION OF BULLETS AND CARTRIDGE CASES.—Experiments have been made to find out with what degree of accuracy it is possible to identify bullets and cartridge cases.

In one such case a man had been shot, and a 380-lead bullet was recovered from his body at the post-mortem examination. On the man suspected of shooting him a 380-revolver was found. The question was—had this bullet been fired from this revolver? We fired about 24 rounds out of the revolver into water so that they should not be deformed, and proceeded to examine them. In diameter, the number of lands or grooves, and the width and pitch of the lands, all the experimental bullets corresponded with the suspected bullet. A closer examination of the bullets under the microscope showed that on all of them were certain small scratches, too small to be seen with the naked eye, but sufficiently well marked or characteristically placed with reference to one or other of the lands to make one fairly certain that all the bullets had been fired from the same revolver. A comparison of these scratches under a comparison microscope settled the question, as the scratches in many of the lands exactly corresponded when seen together under this instrument, and no scratch which could be found on all the experimental bullets was absent on the suspected bullet. The comparison microscope is an instrument by which two bullets each placed under a separate microscope can be viewed simultaneously as if placed side by side. (*Cf.* Stirling, ANALYST, 1933, **58**, 684.)

As a test of the accuracy of this method the police fired 24 bullets out of four revolvers, all of the same make and pattern, numbered the bullets haphazard, kept the key as to which had been fired out of which revolver, and sent the bullets to us. We found no difficulty in sorting out the bullets into four lots, and in every case we were correct.

In one case the question was asked—had a certain small hole in a blood-stained cloth been made by a bullet or by other means. The part of the cloth round the hole was soaked with blood, and this obscured any of the markings which we have previously shown (Annual Report for 1931: ANALYST, 1932, 57, 718) to be characteristic of bullet holes. Analysis of a portion of the cloth, cut from the edges of the hole, showed the presence of lead, and analysis of other equally blood-stained parts of the cloth did not show any lead, so that there was good evidence that the hole in question had been caused by a leaden object having been forcibly pushed through the cloth, and with little doubt this object was a bullet.

IDENTIFICATION OF TYPESCRIPT.—The work reported in the annual report for 1932 (ANALYST, 1934, 39) on the identification of typescript with the typewriter on which it has been produced has also been continued, with the assistance of the police, and the accuracy of the method described has been put to a test as severe as we could make it. By the kindness of one of the firms who sell typewriters, 24 specimens of typescript were obtained from 12 machines, all brand new, all with the same sort of ribbons on the same paper, and all typed by the same typist, who was an expert at typing. When examined either with the naked eye or under a microscope they all looked perfect and identical, except six in which we found slight variations in one of the letters after prolonged examination. In the remaining 18 no differences could be seen, and in all of them the alignment of all the letters was, to ordinary observation, perfect. By microscopic measurement, however, of the alignment of about 200 of the nine commonest letters (E T A O I N S R H) in each of the 18, we were able to sort out 9 pairs, and a reference to the key, which had been kept locked up, showed that all the pairs were correct. The method is very tedious, but, given the time and patience and a sufficiency of the specimen of typescript, appears to be very reliable.

New U.S. Pharmacopoeial Standards for Cod Liver Oil*

THE new U.S.P.X.† (1934) Standards for vitamins *A* and *D* and Vitamin Assays have just been published. These have been developed through a series of conferences with the vitamin experts of the United States and an extensive study of the general standard by the Sub-Committee on Organic Chemicals. The vitamin standards and vitamin assays represent the studies and conclusions of the U.S. Pharmacopoeial Vitamin Advisory Board. The "release" of this announcement, as an interim revision, has been authorised by the U.S.P. Committee of Revision and U.S.P. Board of Trustees, the standards to become official on January 1, 1935.

The U.S.P. Vitamin Advisory Board also recently announced the "release" of "Reference Cod-liver Oils" of known vitamin *A* or vitamin *D* potency, expressed in U.S.P.X. (1934) Units. These "Reference Oils" are to be used as standards in vitamin *A* or *D* assays for determining the potency of Cod-liver Oil, Cod-liver Oil Concentrates, irradiated ergosterol or other irradiated products, or products containing vitamin *A* or vitamin *D*, whether medicines or foods. This Reference Oil is obtainable in 30-ml. containers and is standardised for either its vitamin *A* or vitamin *D* potency. The price per package of either the vitamin *A* or vitamin *D* standard is $2.50.

THE NEW U.S.P.X. COD-LIVER OIL STANDARDS

Minimum standard for Vitamin A *for U.S.P. Cod-liver Oil.*—The minimum Vitamin *A* standard for U.S.P. Cod-liver Oil shall be not less than 600 U.S.P. (1934) Vitamin *A* Units or its equivalent, 600 International Vitamin *A* Units.

Minimum standard for Vitamin D *for U.S.P. Cod-liver Oil.*—The minimum Vitamin *D* standard for U.S.P. Cod-liver Oil shall be not less than 85 U.S.P. (1934) Vitamin *D* Units or its equivalent, 85 International Vitamin *D* Units.

One "United States Pharmacopoeia Unit of Vitamin *A*" is equal in growth-promoting and anti-ophthalmic activities for the rat, to one International Unit of Vitamin *A*, as defined and adopted by the Conference of Vitamin Standards of the Permanent Commission on Biological Standardisation of the League of Nations in June of 1931; one "United States Pharmacopoeia Unit of Vitamin *D*" is equal, in anti-rachitic potency for the rat, to one International Unit of Vitamin *D* as defined and adopted by the Conference of Vitamin Standards of the Permanent Commission on Biological Standardisation of the League of Nations in June of 1931.

The Relation of the New U.S.P. Cod-liver Oil Vitamin Units to Other Units now in Use.—One of the valuable contributions made by the U.S.P. Vitamin Advisory Board in its study of assay reports submitted by many laboratories, when determining the potency of the U.S.P. Reference Cod-liver Oil, was an approximate relationship between the new U.S.P.X (1934) Units for Vitamins *A* and *D* (it should be remembered that these units are identical with the International Units) and other Vitamin Units now referred to on labels and in the literature.

These conversion factors have been published by the Vitamin Board with the hope that they may help to clarify the existing confusion due to the use of so many unofficial units, and with the hope that hereafter in the U.S.A. all vitamin *A* and *D* values will be expressed in the new U.S.P. Units.

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* To become official January 1, 1935.

† U.S.P.X. came into force in January, 1926; the U.S.P.X., 1934, is a revision, not a new edition.—ED.

These conversion factors should not be considered as having any official recognition. They are probably not absolutely exact and are given for information only.

CONVERSION FACTORS FOR VITAMIN *A* AND *D* UNITS

Vitamin A *Units*

One U.S.P.X Vitamin A *Unit,* 1 *"Sherman Unit"* or 1 *A.D.M.A. Vitamin* A *Unit* are each approximately the equivalent of 1·4 International Vitamin *A* Units or 1·4 U.S.P.X (1934) Vitamin *A* Units.

The new U.S.P. minimum standard of 600 *U.S.P.X* (1934) *Vitamin* A *Units* per grm. of Oil is approximately the equivalent of

420 U.S.P.X (1926) VITAMIN *A* UNITS

Vitamin D *Units*

One Steenbock Unit of Vitamin D is approximately the equivalent of 2·7 International or U.S.P.X (1934) Units.

One International Vitamin D *Unit or* 1 *U.S.P.X* (1934) *Vitamin* D *Unit* is approximately the equivalent of

3·25 A.D.M.A. VITAMIN *D* UNITS

One International Vitamin D *Unit* or 1 *U.S.P.X* (1934) *Vitamin* D *Unit* is approximately the equivalent of

1·66 OSLO VITAMIN *D* UNITS

The new U.S.P. minimum standard of 85 *U.S.P.X.* (1934) *Vitamin* D *Units* per grm. of Oil is approximately the equivalent of

31·5 STEENBOCK UNITS
276 A.D.M.A. UNITS
142 OSLO UNITS.

Copies of the U.S.P.X (1934) interim revision of Cod-liver Oil Tests or the Reference Cod-liver Oil may be obtained by addressing the Chairman of the Committee of Revision.

E. FULLERTON COOK

FORTY-THIRD STREET AND WOODLAND AVENUE
PHILADELPHIA, PA.

International Atomic Weights, 1934*

	Symbol.	At. No.	At. wt.		Symbol.	At. No.	At. wt.
Aluminium	Al	13	26·97	Neodymium	Nd	60	144·27
Antimony	Sb	51	121·76	Neon	Ne	10	20·183
Argon	A	18	39·944	Nickel	Ni	28	58·69
Arsenic	As	33	74·91	Niobium	Nb		
Barium	Ba	56	137·36	(Columbium)	(Cb)	41	93·3
Beryllium	Be	4	9·02	Nitrogen	N	7	14·008
Bismuth	Bi	83	209·00	Osmium	Os	76	191·5
Boron	B	5	10·82	Oxygen	O	8	16·0000
Bromine	Br	35	79·916	Palladium	Pd	46	106·7
Cadmium	Cd	48	112·41	Phosphorus	P	15	31·02
Caesium	Cs	55	132·91	Platinum	Pt	78	195·23
Calcium	Ca	20	40·08	Potassium	K	19	39·096
Carbon	C	6	12·00	Praseodymium	Pr	59	140·92
Cerium	Ce	58	140·13	Radium	Ra	88	225·97
Chlorine	Cl	17	35·457	Radon	Rn	86	222
Chromium	Cr	24	52·01	Rhenium	Re	75	186·31
Cobalt	Co	27	58·94	Rhodium	Rh	45	102·91
Copper	Cu	29	63·57	Rubidium	Rb	37	85·44
Dysprosium	Dy	66	162·46	Ruthenium	Ru	44	101·7
Erbium	Er	68	167·64	Samarium	Sm	62	150·43
Europium	Eu	63	152·0	Scandium	Sc	21	45·10
Fluorine	F	9	19·00	Selenium	Se	34	78·96
Gadolinium	Gd	64	157·3	Silicon	Si	14	28·06
Gallium	Ga	31	69·72	Silver	Ag	47	107·880
Germanium	Ge	32	72·60	Sodium	Na	11	22·997
Gold	Au	79	197·2	Strontium	Sr	38	87·63
Hafnium	Hf	72	178·6	Sulphur	S	16	32·06
Helium	He	2	4·002	Tantalum	Ta	73	181·4
Holmium	Ho	67	163·5	Tellurium	Te	52	127·61
Hydrogen	H	1	1·0078	Terbium	Tb	65	159·2
Indium	In	49	114·76	Thallium	Tl	81	204·39
Iodine	I	53	126·92	Thorium	Th	90	232·12
Iridium	Ir	77	193·1	Thulium	Tm	69	169·4
Iron	Fe	26	55·84	Tin	Sn	50	118·70
Krypton	Kr	36	83·7	Titanium	Ti	22	47·90
Lanthanum	La	57	138·92	Tungsten	W	74	184·0
Lead	Pb	82	207·22	Uranium	U	92	238·14
Lithium	Li	3	6·940	Vanadium	V	23	50·95
Lutecium	Lu	71	175·0	Xenon	Xe	54	131·3
Magnesium	Mg	12	24·32	Ytterbium	Yb	70	173·04
Manganese	Mn	25	54·93	Yttrium	Y	39	88·92
Mercury	Hg	80	200·61	Zinc	Zn	30	65·38
Molybdenum	Mo	42	96·0	Zirconium	Zr	40	91·22

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* Reproduced by permission of the Chemical Society. Copies of this table printed on cards can be obtained on application to the Assistant Secretary, Chemical Society. Price 2d. each. (*cf.* ANALYST, 1934, 414).

Medical Research Council*

THE CHEMISTRY OF FLESH FOODS AND THEIR LOSSES ON COOKING

SINCE practically all the existing analytical figures for flesh foods refer to uncooked foods, the Medical Research Council made grants to the authors of this report for systematic analyses of the cooked foods, and the scope of the work was gradually extended into a thorough investigation of the composition of flesh foods.

Part I (pp. 43) gives full details of the scheme of analysis evolved, including the determination of total nitrogen, non-protein nitrogen, extractive nitrogen, fat, carbohydrate, chlorides, total and inorganic phosphorus, sodium, potassium, calcium, magnesium, and iron. The system is applicable to any *animal* material.

Micro-analytical methods have been used, even when large amounts of material were available and large samples were originally taken, and the technique throughout is described in detail.

Errors of sampling have been shown to be relatively small, and fortuitous analytical errors to be equally small; hence, analytical work has not been duplicated, except for total nitrogen, when small samples of heterogeneous material have had to be taken.

Representative samples of meat were obtained by cutting up the material with a stainless-steel knife and thoroughly mixing the fragments. Fat and lean were analysed separately. Fish flesh was broken up with a fork until sufficiently homogeneous for sampling without mincing or grinding. Separate analyses were made of gravies and drippings.

Tables (pp. 48–65) are given showing the composition of all the fish and meat foods examined; all were in the cooked state, except in the comparatively few instances where the foods are eaten raw. The various cuts are arranged alphabetically under the name of the meat, not of the animal. Eggs are included among animal organs.

Formulae have been worked out for calculating how much of any constituent could be obtained from 100 grms. of the food as served, or from 100 grms. of the raw food. Thus, if a piece of meat weighed R grms. when raw, and C grms. when cooked, E grms. were edible, and the edible portion contained x grms. of some constituent, then the amount of this constituent in 100 grms. of edible portion will be

$$\frac{100x}{E} = A$$

and the amount that can be obtained from 100 grms. of the food as served will be

$$\frac{100x}{C} = B.$$

The multiplying factor (F_1) to convert A (the figure given in the tables) into B, will be

$$\frac{B}{A} = \left(\frac{100x}{C}\right) \div \left(\frac{100x}{E}\right) = \frac{E}{C}$$

i.e. F_1 is the ratio of the weight of the edible portion to the weight of the cooked meat. In the same way it may be shown that F_2 is the ratio of the weight of the edible portion to the raw weight. It is also possible with the aid of the factors F_1 and F_2 to calculate the amount of the various loss which may take place in the cooking and serving of the food.

FACTOR FOR PROTEIN.—It has repeatedly been shown that the factor 6·25 is not the correct one, and it would therefore be better if this factor were given up and only the figure for protein nitrogen were used. In the present tables, however, both the total and the protein nitrogen have been determined, and the latter has been multiplied by 6·25 for the benefit of those who expect to see a figure for protein.

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* By R. A. McCance and H. L. Shipp. pp. 146. London: H.M. Stationery Office. Special Report Series. No. 187. Price 2/6 net.

PURINE NITROGEN.—The present results tend to confirm such previous figures as are available, but these constituents have not previously been determined in many of the materials now examined, and the results are interesting.

	Purine nitrogen per 100 grm. of edible substances Grm.	Purine nitrogen per 100 grms. of total nitrogen Grms.
Beef (general average)	0·081	1·70
Mutton ,, ,, ...	0·063	1·57
Pork ,, ,, ...	0·069	1·58
Birds ,, ,, ...	0·094	1·97
Brains	0·033	1·60
Hearts	0·166	2·80
Livers and kidneys (average) ..	0·140	3·00
Sweetbreads	0·426	11·50
Flat fish (miscellaneous)	0·059	1·85
Gadoids	0·069	2·06
Other demersal fish	0·069	2·00
Whiting	0·092	2·94
Cod's roe (hard)	0·120	3·30
Herring (no roes)	0·150	4·00
Sprats (smoked and fresh, average)..	0·180	4·60
Sardines	0·234	6·80
Whitebait	0·323	10·30
Herring roe (soft)	0·484	11·90

INORGANIC SALTS.—The percentage of soluble salts in meat and flesh is not greatly changed by cooking; boiling may lower the percentage a little, roasting and frying raise it.

The sodium varied, as a rule, between 50 and 120 mgrms. per 100 grms. of cooked material, and was slightly higher in fish than in meat. There appears to be more sodium present than is required to account for the chlorine as NaCl. This is attributed to the facts that: (i) some of the sodium in serum and intercellular fluids is present as bicarbonate; (ii) muscle fibres adsorb sodium ions loosely on to their external surfaces.

The figures for potassium range, as a rule, between 200 and 400 mgrms. per 100 grms.

LOSSES ON COOKING.—Part II deals with the methods of studying the cooking of meat and its accompanying losses. Many of the results are expressed in graphical form. Experiments described show that there is no evidence that a pellicle forms on the outside of a joint when cooking begins at a high temperature. Unless, therefore, the procedure can be supported on grounds of palatability or digestibility, there seems to be no reason why an oven should be raised to a high temperature before the joint is inserted, or why the water should be boiling before the meat is put in. Both would appear, indeed, to be a waste of heat. When fully cooked, beef has been found to lose the same amount of weight and to show the same loss of water and salts. Egg proteins do not shrink when heated to 100° C. The extent of the shrinkage of beef, fish, kidney and liver proteins is but little affected by raising the temperature from 80° to 100° C., but is slightly increased by raising the temperature from 100° to 120° C. Brain does not shrink below 80° C., but does so at higher temperatures. Fish muscle tends to lose weight if soaked in aqueous solutions below about p_H 5·6. Acids and alkalis inhibit heat shrinkage of muscle proteins. In fish shrinkage tends to be greatest between p_H 4·0 and 4·5 (where loss of weight on soaking is greatest); in meat maximum shrinkage occurs at p_H 6. It is suggested that the predominating protein in fish has a more acid iso-electric point than that of beef.

Shrinkage on heating muscle proteins is more rapid and extensive 40 hours after death than it is immediately after the animal has been killed. After steam-heating, the percentage loss of water always agrees with that of the soluble salts. Fifty per cent. of the water and salts in beef may thus be lost, and a still higher percentage in kidneys. The percentage loss of water always exceeds the percentage loss of weight, but the relationship between the losses depends upon the loss of the other constituents. On lowering the p_H of the cooking medium, meat and fish tend to lose more of their cations and less of their anions; on raising the p_H the reverse takes place. The expressed juices of fish are more alkaline than those of beef. In roasting, the loss of water is nearly all due to evaporation, the loss of salts (which are left on the surface of the meat) being small. The loss of salts can be increased by reducing evaporation. Frying in deep fat leads to such rapid evaporation of water from the surface that the loss of salts is reduced to a minimum. The loss of protein is more complicated than that of salts, because there are several sources of loss. The loss is slightly greater on boiling than on steaming, and is greater at 120° C. than at 100° C. Kidneys lose a higher percentage of their proteins than other organs, and losses up to 20 per cent. have been observed. The loss of fat on cooking is due to liquefaction by heat; shrinkage of the proteins has little influence on the loss of fat.

The pamphlet concludes with a bibliography occupying 6 pages.

The National Physical Laboratory

METROLOGY DEPARTMENT

TESTS ON VOLUMETRIC GLASSWARE*

No fundamental changes have been made from the preceding edition, but several points have been dealt with in more detail, as, for example, the testing of burette taps and permissible schemes of subdivision of scales on graduated glassware.

The contents of the pamphlet are as follows:—Tests undertaken. Transmission and insurance of apparatus.

Regulations Governing Class A Tests.†—Laboratory marks and certificates—Units of volume—General conditions and methods of test—Flasks—Pipettes—Burettes—Graduated pipettes—Graduated cylinders—Density—Bottles and pyknometers—Vessels for gas analysis—Standard volumetric glassware for testing tar and its products—Other apparatus.

Regulations Governing Class B Tests.‡—Laboratory marks and certificates—Units of volume—General conditions and methods of test—Flasks—Pipettes—Burettes—Graduated pipettes—Graduated cylinders—Vessels for gas analysis—Standard volumetric ware for testing tar and its products—Vessels for milk testing—Other apparatus.

Printed forms for use as advice notes, to be sent in respect of each consignment, may be obtained on application to the Director. The use of these forms instead of a firm's ordinary advice notes is optional, but is recommended.

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* New Edition. Pp. 28. April, 1934. Copies may be obtained free of charge on application to The Director, National Physical Laboratory, Teddington, Middlesex.

† The examination of vessels intended to possess the highest accuracy.

‡ The examination of vessels intended to possess only commercial accuracy.

Copies of a separate pamphlet, entitled "Tests on Volumetric Glass Ware used in Dairy Chemistry," may be obtained on application to the Director.

The present pamphlet concludes with a list of verification fees and other charges, and with schemes of sub-division and numbering for intervals of 1 ml., 2 ml. and 5 ml. or decimal multiples or sub-multiples thereof.

Full particulars relating to certificates, reports and statements, insurance and custody of instruments, terms of payment, etc., will be found in the "General Regulations," issued separately and obtainable upon application to the Director.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs Analysis

Detection of Gelatin in Cultured Buttermilk and Cottage Cheese. G. A. Richardson and N. P. Tarassuk. (*J. Assoc. Off. Agric. Chem.*, 1934, **17**, 314–319.)—The Stokes test (ANALYST, 1897, **22**, 320), which is the official method of the Association, gives erroneous results with sour milk or cream, cultured buttermilk and cottage cheese, owing presumably to the presence of products resulting from the effect of heat, acidification or proteolysis on the proteins; the various modifications suggested (see Mendelsohn, *id.*, 1930, **55**, 567) are not entirely satisfactory. Addition of picric acid produces a precipitate (which is particularly voluminous with cottage cheese made from rennet) even in the presence of gelatin, and this is attributed to derived proteins which mercuric nitrate does not remove. In applying the test to cultured buttermilk, therefore, the sample is stirred thoroughly at 25° C., 10 ml. are shaken with 10 ml. of mercuric nitrate solution, and the mixture is filtered after it has been allowed to stand for 5 minutes (No. 1 filtrate). The reagent, which must be free from mercurous ions, is prepared by dissolving mercury in twice its weight of nitric acid and diluting the solution to 25 times its volume with water. An aliquot part of filtrate No. 1 is mixed with half its volume of a saturated solution of picric acid, and the type of precipitate, if any, is noted; the remainder of the filtrate is cooled in ice-water and shaken well with half its volume of a 20 per cent. solution of trichloroacetic acid, left for 16 hours at 8° to 10° C., with occasional shaking, and the precipitate is again noted. The mixture is filtered, and the filtrate is warmed at 50° to 55° C. for at least 5 minutes, and is observed at this temperature after addition of half its volume of a warm solution of picric acid saturated at 50° C. With cottage cheese, 5 grms. are extracted with 10 ml. of water at 50° to 60° C., and the extract is treated with 5 ml. of mercuric nitrate reagent as before; the resulting precipitate is then removed after 5 minutes, and the filtrate is treated with 5 c.c. of the mercuric nitrate solution, after which the above procedure (addition of picric acid, etc.) is followed. Tables illustrate the observations and conclusions at each stage, but it is advisable to carry out control experiments simultaneously. It is evident that cultured butter-milk and cottage cheese (especially when made with rennet) contain derived proteins which are not removed completely by mercuric nitrate, but which with picric acid give a flocculent precipitate with a clean serum, as distinct from the turbidity due to gelatin picrate. Under the conditions described these, but not gelatin, are removed by trichloroacetic acid as a flocculent precipitate with a clear serum, so that subsequent addition of picric acid clearly distinguishes those samples which contain gelatin; 0·1 to 0·25 per cent. produces a cloudy solution, and greater amounts a yellow precipitate. Trichloroacetic acid also causes coagulation of derived proteins, which may then be removed by filtration and the picric acid test applied to the clear serum. The alternative method of Jacobs and Jaffe (*Ind. Eng. Chem., Anal. Ed.*, 1932, **4**, 418) gives excellent results with fresh samples for which rennet has not been used, but otherwise requires modifying by the introduction of precipitation with trichloroacetic acid. J. G.

Detection of Soya Bean Flour in Manufactured Foods. C. H. La Wall and J. W. E. Harrisson. (*J. Assoc. Off. Agric. Chem.*, 1934, **17**, 329–334.)—Soya bean flour (2 to 15 per cent. of the wheat flour used, or 2 to 10 per cent. of the finished food) has been stated to improve the flavour, food value, appearance, yield, lasting value, binding- shortening- and egg-requirements of bakery and sausage products. Tests are as follows:—(i) A strip of red litmus paper is partly immersed in a mixture of 0·5 grm. of sample with 5 ml. of a 2 per cent. solution of urea, contained in a stoppered tube, which is heated at 40° C. for 3 hours. Liberation of ammonia by the urease in soya bean flour produces a blue colour. (ii) Bromphenol blue also gives a blue colour at the end of the heating period. (iii) For quantitative work (*cf. Chem. Weekblad*, 1916, **13**, 254) a mixture of 150 mgrms. of the sample with 10 ml. of a 1 per cent. solution of urea is warmed in a stoppered test-tube for 30 minutes at 25° C., and is then titrated with 0·1 *N* sulphuric acid, with methyl orange as indicator. (iv) For work on the micro-scale (*e.g.* with pea-nut butter), the oil is extracted with ether, and about 2 grms. of the residue are mixed in a small porcelain crucible with a 2 per cent. solution of urea. The crucible is at once covered with a slide, on the underside of which hangs a drop of 10 per cent. hydrochloric acid, and is placed overnight in a warm place; any crystals of ammonium chloride are identified in the usual way. (v) A stiff paste of the flour with 5 per cent. potassium hydroxide solution appears yellow in the presence of soya bean flour. (vi) The supernatant liquid and residue obtained on shaking 1 grm. of the ground sample with 10 ml. of petroleum spirit are coloured yellow if soya flour is present; 5 per cent. gives a yellow spotted residue. (vii) A paste of wheat flour with concentrated hydrochloric acid develops a lavender colour much more rapidly if soya flour is present. (viii) Microscopical features are the characteristic hour-glass shaped cells of the sub-epidermal layer of the bean and the yellow colour of the aleurone-containing cells after treatment with a solution of iodine. Test (i) gave negative results for all of the cereals and legumes tested which did not contain soya flour (10 out of 24), and (ii) confirmed these results except with soup beans, where the reaction was faintly positive. Test (iii) gave titration figures of 0·2 or less, 0·75 or less, 19·20 to 23·00, 3·10 to 10·40, and 33·10 ml. of 0·1 *N* acid for cereals, legumes (excepting soya and jack beans), whole soya beans, soya flours, and jack beans, respectively; 2 and 5 per cent. of soya flour in semolina and in unsmoked sausage, respectively, were detectable by (i), but unsatisfactory results were obtained with cakes prepared with chemical leavening agents. With Test (iv) a few crystals of ammonium chloride were obtained even in control experiments, and these were attributed to spontaneous decomposition of the urea solution. J. G.

Presence of Methyl Alcohol in Alcohols from Wine, including Marc Wine and Fruit Wine. M. Flanzy. (*Compt. rend.*, 1934, **198**, 2020–2022.)—By the method previously described (ANALYST, 1934, 193), determinations have been made of the proportions of methyl alcohol in a number of potable spirits; the results are expressed as mgrms. of methyl alcohol per litre of total alcohol. For wine spirit and weak wine spirit (trois-six), the values are always less than 1000; here and in other cases also, the trois-six show slightly the higher figures. Marc spirit and weak marc spirit give 1000 to 2000; weak piquette (second cuvé) spirit, usually about 2000, but in one instance almost 4000; cognac, 300 to 400 for Hennessy, Martell and Boulestin brands, 500 to 800 for "self" samples, and 1500 for a piquette spirit; armagnac, 500 to 800; kirsch, mirabelle, and quetsch, 1200 to 1600; calvados, 300 to 1200 for distillery products, and 750 to 1600 for propriétaire products; perry spirit, 660 to 750; cider marc spirit, about 6000. For one and the same kind of fruit, the nature of the soil, the climate and the vintage have no marked influence on the proportion of methyl alcohol found. T. H. P.

New Pentabromoacetone Process for determining Citric Acid in Wine. P. Berg and G. Schulze. (*Z. Unters. Lebensm.*, 1934, **67**, 605–613.)—The oxidation of citric acid to acetonedicarboxylic acid and the determination of this as pentabromoacetone gives highly accurate results with pure aqueous solutions of the acid, provided that certain conditions are observed, but the presence of other organic compounds, as in wine, introduces disturbing factors (*cf.* Kogan, *Z. anal. Chem.*, 1930, **80**, 112; Täufel and Mayr, *ibid.*, 1933, **93**, 1; Bartels, ANALYST, Abstr., 1933, **58**, 164). The authors have modified the process in the following directions: (i) The additions of permanganate, potassium bromide, and sulphuric acid are adjusted to the extract-content of the wine. (ii) The oxidation and bromination are carried out in presence of ammonium sulphate, which assists the formation and separation of the pentabromoacetone, even when the content of citric acid is low. (iii) The optimum temperature of this reaction is established as 15° C. and the optimum time as 1 hour; no attempt must be made to hasten the reaction by mechanical means. (iv) Precautions in the addition of the ferrous ammonium sulphate for removing the manganese oxide precipitate are indicated. (v) Slight modifications are made in the conditions of titration given by Kometiani (ANALYST, 1932, **57**, 192). Detailed instructions are given for the procedure to be followed with wines of different characters.

The permissible additions of citric acid to wine or must in various European countries are stated. No such addition is allowed in Germany—where treatment with potassium ferrocyanide is legal—and the German wines examined contained not more than 0·2 grm. of citric acid per litre. In most other countries from 0·5 to 1 grm. of the acid may be added per litre, although in Greece no limit is fixed. White Bordeaux often contains more than 2 grms. of the acid (in one instance 3·7 grms. were found) per litre. T. H. P.

Simple Method for the Purification of Citrus Pectin. H. R. Nanji and J. J. Chinoy. (*Biochem. J.*, 1934, **28**, 456–462.)—Pectin which has been derived from *Citrus* fruits and contains 90–95 per cent. of pectin, can be further purified by treatment with bromine or iodine solutions at temperatures between 20° and 40° C. To 50 ml. of pectin solution (0·5 per cent.) in water, 3 ml. of *N*/10 iodine or 5 ml. of *N*/10 bromine are added, and the mixture is allowed to stand for about 12 hours at 20° C. or 2 hours at 40° C. The excess of halide is then removed by extraction with ether or by aeration at 40° C., after which the pectin is precipitated with 95 per cent. alcohol, filtered off and dried at 100° C. for 20 hours. Chlorine water, under similar conditions, causes the breakdown of the pectin, and dilute hydrogen peroxide has no action. The halogens have little action on pectic acid or sodium pectate. The yields of furfuraldehyde and carbon dioxide from the purified products agree with the accepted figures for a purified pectin, and the methoxyl-content approaches the theoretical value for a fully methoxylated pectic acid. S. G. S.

Component Fatty Acids and Glycerides of the Milk-Fat of Indian Camels. D. R. Dhingra. (*Biochem. J.*, 1934, **28**, 73–78.)—The component fatty acids and glycerides of the milk-fat of the camel have been studied in detail in order to compare them with those of the milk-fats of the cow, buffalo, sheep and goat. In north-western parts of India milk from camels is utilised as an article of diet by some tribes, but the fat is rarely extracted from the milk and used as a substitute for "ghee." It is shown that the fatty acids of the milk-fat of the camel differ from those of cow, buffalo, goat and sheep milk-fats in a lower content of fatty acids volatile in steam. Camel milk-fat can, to a great extent, be distinguished from the milk-fats of other animals by its lower Kirschner and Reichert-Meissl values. The amount of the lower fatty acids is in decreasing order in the milk-fats of the sheep, goat, cow, buffalo and camel. The content of the fully-saturated glycerides in camel milk-fat is a function of mean unsaturation, like that of the milk-fats of other animals. The component fatty acids of the fully-saturated glycerides of camel milk-fat are in proportions somewhat different from those in the milk-fats hitherto studied. The composition of the fatty acids of the mixed saturated-unsaturated glycerides of camel milk-fat is little different from that of most cow and buffalo butters, but more so from that of goat and sheep milk-fats; the latter show a higher percentage of the butyric-lauric group of acids and a correspondingly lower proportion of unsaturated acids. From the point of view of general properties and of the component glycerides present, there seems no reason why camel milk-fat should not be used as a substitute for cow, buffalo, *etc.*, milk-fats. The general characteristics of the milk-fat were as follows:—Acid value, 0·2; saponification equivalent, 259; iodine value, 40·8; Reichert-Meissl value, 16·4; Polenske value, 1·6; Kirschner value, 14·3; solidification point, 35·3° C.; n_D^{40}, 1·4555. The component acids of the fully-saturated glycerides were: Butyric, 3·4; caproic, 1·0; caprylic, 0·1; capric, 2·1; lauric, 2·2; myristic, 18·4; palmitic, 55·0; and stearic acid, 17·8 per cent. P. H. P.

Influence of Salts used in Curing on the Oxidation and Yellowing of Lard. C. H. Lea. (*J. Soc. Chem. Ind.*, 1934, **53**, 182–184T.)—To investigate the effect of salts used in curing on the rate of oxidation of lard, the freshly-rendered leaf fat was pipetted into flat-bottomed crystallising dishes, and allowed to solidify, and the required salt solution was added so that the depths of the layers were 1·5 and 3·5 mm., respectively. A synthetic bacon pickle was used containing in 100-ml., sodium chloride 26·0 grms., potassium nitrate 3·5 grms., and potassium nitrite 0·03 grm. Seven dishes of one kind were placed in each of a number of glass-stoppered jars (to prevent loss by evaporation) and stored in the dark at 20° C. To examine the fat, the aqueous layer was poured off, the fat was washed with water and dissolved in ether; the solution was washed 3 times with water, and dried over sodium sulphate, and the solvent was removed *in vacuo* at 50° C. Results showed that the salts used in pickles for curing bacon have a very pronounced accelerating effect on the oxidation of pork fat. A rancid flavour usually appears in the fat at peroxide-oxygen values of the order 8 to 10 ml. per grm. It was found that after the induction period the fat under water oxidised more rapidly than that under the salt solution, possibly owing to the reversal of the catalytic effect of the salts, or to the reduced solubility and rate of diffusion of oxygen in the concentrated solution. The nitrite appeared to have little influence when added to the chloride and nitrate in quantity up to 0·15 per cent., but had a slight accelerating effect at 1 per cent. D. G. H.

Fractional Extraction of Soya-Bean Oil and the Drying Properties of the Fractions. T. Yamada. (*J. Soc. Chem. Ind. Japan, English Abstr.*, 1934, **37**, 190–192B.)—Soya-bean oil has been fractionated as follows:—100 grms. of the oil were dissolved in an equal quantity of acetone, and the solution was chilled at −20° C. On standing for a short time at this temperature a butter-like mass separated out. The clear liquid was decanted. The residual oil was dissolved in 100 ml. of acetone, and the chilling and decanting processes were repeated. Ten fractions were thus obtained with iodine values (Wijs) ranging from 152 to 100, the original oil having an iodine value of 137. The drying powers of the fractions, tested by measuring the gain in weight of the oils spread on glass plates and exposed to the air over a period of about 50 days, were in proportion to the degree of unsaturation, a maximum in the weight increment-time curve for oil of iodine value 145 and for the original oil occurring at about 27 days and 42 days, respectively. S. G. C.

Adulteration of Aloes. E. Léger. (*J. Pharm. Chim.*, 1934, **126**, 533–535.)—A well-prepared sample of powdered aloes is entirely soluble in officinal (French Codex) ammonia diluted with nine times its volume of water, and a use of this fact will disclose adulteration. The tests for aloes given in the French Codex are sensitive with samples adulterated to the extent of 50 per cent.; Klunge's reaction, however (red colour given by iso-barbaloin with copper sulphate in presence of sodium chloride and alcohol), is positive in the sample containing 10 per cent. of Barbadoes or *Curaçao* aloes. Treatment with ammonia should be followed by treatment with benzene, which dissolves rosin but scarcely any aloes. Klunge's reaction will distinguish the Cape aloes type from aloes from Antilles, Curaçao, Barbadoes, etc. If the quality and purity of the sample are to be determined, no test will take the place of the determination of the chlorinated aloines. This determination will detect adulteration of the more expensive Curaçao type (containing 31 to 34 per cent. of the aloines) with the cheaper Cape type containing 17 to 20 per cent. D. G. H.

Colour Reaction of Mono-carboxylic Chrysanthemic Acid (from the Hydrolysis of Pyrethrin I). M. Audiffren. (*J. Pharm. Chim.*, 1934, **126**, 535–536.)—Monocarboxylic chrysanthemic acid in aqueous concentration of about 1 in 1000 to 1 in 10,000 gives no reaction with Denigès' reagent, but in a sulphuric acid medium, a reaction occurs, sensitive to 1 part in 100,000 of the acid. One ml. of the Denigès' reagent is added to 1 ml. of the dilute chrysanthemic acid solution, followed by 0·4 to 0·5 ml. of concentrated sulphuric acid, poured in rapidly so that the acid sinks to the bottom of the tube. After a few seconds the liquid is mixed, and, after a momentary contact, a pink or red colour develops, changing to violet and then green. After 24 hours a yellow precipitate is formed. If the sulphuric acid is added, drop by drop, the reaction is less sensitive. A positive reaction was obtained with the first fractions of the distillate from the urines of patients treated by pyrethrin employed as an anthelmintic, and it appears that pyrethrin I is rapidly eliminated in the urine, giving, among other products of decomposition, monocarboxylic chrysanthemic acid. D. G. H.

Detection of Very Small Quantities of Nicotine. A. Wenusch. (*Z. Unters. Lebensm.*, 1934, **67**, 601–605.)—Various reactions which have been suggested for the detection of nicotine are unsuitable for this purpose, as they are reactions of impurities or decomposition products of the nicotine. Several new reactions now described admit of the identification of nicotine in very small quantities. A liquid material is acidified slightly with dilute sulphuric acid and concentrated on a water-bath. The residue, or a solid product to be tested, is made strongly alkaline with cold concentrated sodium hydroxide solution and either repeatedly and vigorously shaken with petroleum spirit or extracted in a Soxhlet apparatus. The petroleum spirit extract is shaken with about 5 ml. of dilute sulphuric acid (1:20), which takes up any nicotine as sulphate. If a drop of the acid solution gives no precipitate or opalescence with silicotungstic acid solution, nicotine is absent. In the opposite case, the 5 ml. of acid are treated with 5 ml. of concentrated potassium hydroxide solution and distilled from a ceresine bath (up to 170° C.). The distillate is tested as follows to identify the nicotine.

(1) Two ml. are boiled for some minutes with a few crystals of 2 : 4-dinitrochlorobenzene, cooled and treated with alcoholic 1 per cent. potassium hydroxide in excess; a violet colour indicates the presence of a pyridine nucleus. (2) This is confirmed by treating a few drops of the distillate on a porcelain plate with Selmi's reagent (potassium platinum iodide), which gives a black precipitate (in presence of 1:10000 of nicotine, after long standing). The remainder of the distillate is made strongly alkaline with concentrated sodium (not potassium) hydroxide and thoroughly shaken with several portions of ether, and the ethereal extract is treated with an ethereal picric acid solution until precipitation is complete (absence of precipitate shows absence of nicotine). The precipitated dipicrate is

collected on a small weighed filter, washed with ether, dried and weighed, and then dissolved in hot water (3 ml. per 0·01 grm. of picrate); the solution, filtered while hot, is left to crystallise and the melting-point of the crystals (about 218° C.) is determined. The nicotine may be further characterised by treating a little of the dipicrate with sodium hydroxide and silver acetate and testing the resulting nicotyrin (i) with a solution of *p*-dimethylaminobenzaldehyde in concentrated phosphoric acid (violet colour), (ii) with vanillin and hydrochloric acid (red colour), and (iii) with quinone in phosphoric acid solution (violet colour). T. H. P.

Biochemical

Biological Value of Proteins. V. The Comparative Biological Value of the Proteins of Whole Wheat, Whole Maize and Maize Gluten, measured by the Growth of Young Rats. M. A. Boas-Fixsen, J. C. D. Hutchinson, and H. M. Jackson. (*Biochem. J.*, 1934, **28**, 592–601.)—The biological value of a protein is measured by the gain in weight per grm. of protein ingested. On this basis the proteins of whole wheat and whole maize in diets containing 9 to 10 per cent. of protein have values of the same order (1·30 to 1·36). These may increase to 1·4 to 1·5 after the food has been cooked. Maize gluten is inferior to the proteins from the whole grain, probably owing to a lower proportion of zein. Results indicate that if the value is

$$\frac{\text{Weight increase in grms.}}{\text{Protein ingested in grms.} - 10}$$

the ratios are constant and independent of the food. This gives 1·85 for wheat and 1·73 for maize at the 9 to 10 per cent. level, with no difference between raw and cooked food. The 10-grm. quantity is regarded as the "maintenance requirement," as distinct from growth needs. S. G. S.

Fat Metabolism in Fishes. III. Selective Formation of Fat-Deposits. J. A. Lovern. (*Biochem. J.*, 1934, **28**, 394–402.)—The examination of fats from various parts of the body of certain fishes reveals the fact that for each one examined, there is a considerable variation in the composition of fatty acids, indicating a highly selective formation of fat-deposits. This paper deals with the liver and peritoneal fats of the conger eel and the fats from depots and organs of the dolphin and porpoise. Fats from the porpoise and dolphin are of a type similar to those from the sperm whale, which is a zoologically related species. For these animals the organ-fats differ from the depot-fats, which contain large quantities of iso-valeric acid. The blubber of a porpoise foetus also contains iso-valeric acid, together with a large amount of highly unsaturated acids. The heart-fat of a porpoise contains acid more unsaturated than those from the liver, which is contrary to the theory that the latter organ acts as a desaturating agent.
S. G. S.

Isolation of Crystalline Stercobilin. C. J. Watson. (*J. Biol. Chem.*, 1934, **105**, 469–472.)—A simpler and more efficient method than that previously described (*Z. physiol. Chem.*, 1932, **204**, 57, **208**, 101; 1933, **221**, 145; and *Proc. Soc.*

Exp. Biol. and Med., 1933, **30**, 1207) has been worked out for the isolation of stercobilin from human faeces. The faeces are ground, mixed with glacial acetic acid to a semi-liquid consistence, and ether is added in sufficient quantity to give a clear supernatant fluid after mixing. The ether is decanted, and the extraction is repeated 15 to 20 times until the extract is of a relatively pale colour, glacial acetic acid being added after every second or third extraction. The greater part of the ether is removed by vacuum distillation, and the acetic acid solution is poured into 6 to 8 volumes of 1 per cent. hydrochloric acid, and left to stand overnight to effect more complete precipitation. The filtrate is covered with a considerable amount of ether, and sufficient sodium acetate is added to make the solution negative to Congo red. After shaking, the extraction is repeated 5 times with smaller amounts of ether, which removes the major portion of the copromesobiliviolin and any porphyrins. The residual aqueous solution is repeatedly extracted with small amounts of chloroform, and this is next extracted many times with water. The filtered aqueous extract is rather strongly acidified with 25 per cent. hydrochloric acid, and the stercobilin may then be obtained as hydrochloride by extraction with chloroform. This solution is superficially dried over anhydrous sodium sulphate, filtered, concentrated, and poured into 15 to 20 volumes of dry petroleum spirit, when there is an almost quantitative precipitation of the hydrochloride, which is re-dissolved in chloroform and re-precipitated. The free substance, possessed of both basic and acidic properties, may be obtained by dissolving the hydrochloride in a small amount of 0·1 *N* sodium hydroxide solution, and this solution is mixed with an equal amount of chloroform, acidified in a separating funnel with a few drops of acetic acid, and shaken. The free stercobilin passes slowly into the chloroform, and the solution, which is dried by filtration through chloroform-moistened paper, is concentrated so that crystallisation takes place. The free substance is much less soluble in hot chloroform than the hydrochloride, and the crystals are of more reddish appearance. The stercobilin thus isolated appears to be identical in every way with that obtained by the original method. From the total amount of faeces for an 8-day period (920 grms.) from a typical case of congenital haemolytic jaundice, 2·2 grms. of crystalline stercobilin hydrochloride were obtained. It seems probable that the hydrochloride crystallises with chloroform of crystallisation, which is lost partly on standing, and more completely on heating; this would account for the colour-changes from the light yellow of the fresh crystals to the yellow-orange of crystals exposed for a short time to the air. D. G. H.

Methyl Alcohol in Foliage Leaves. Relation between the Alcohol and Chlorophyll. M. Flanzy. (*Compt. rend.*, 1934, **198**, 2118–2120.)—The proportion of methyl alcohol in samples of green, and partly and entirely etiolated leaves was determined in the distillate obtained after boiling 1 kilo. of material in water, cooling and distilling. The distillate was suitably concentrated and purified, and the alcohol was determined by the micro method previously described (Analyst, 1934, 193). Methyl alcohol was found in all the samples examined, and a larger proportion was present in the green leaves than in etiolated leaves of a given plant, whilst in the same species the greater the proportion of chlorophyll the larger was the amount of the alcohol found. On 1 kilo. of the dry material the quantity varied from 895 mgrms. of alcohol for etiolated cabbage leaves to 3426 for green chicory leaves, 7174 for dark green nettle leaves, and 4718 for light green nettle leaves. There appears to be a definite methyl alcohol figure for each species, and it remains to be determined whether the figure is a simple function of the chlorophyll activity or of the quantity of chlorophyll present as well. Since there is a relation between the proportion of chlorophyll and the amounts of certain metals present, it may follow that there is a connection between the methyl alcohol-content and the presence of these metals. D. G. H.

Separation of Cysteine from Ascorbic Acid by means of Mercuric Acetate. A. Emmerie. (*Biochem. J.*, 1934, **28**, 268–269.)—A method is described by which cysteine, a source of error in the determination of ascorbic acid by means of 2.6-dichlorophenolindophenol solution, is removed quantitatively with mercuric acetate solution. Van Eekelen, Emmerie, Josephy and Wolff (*Nature*, 1933, **132**, 315) stated that cysteine is precipitated with mercuric acetate, whereas ascorbic acid is reversibly oxidised and can be quantitatively regenerated by means of hydrogen sulphide (see Tillmans, Hirsch and Dick, *Z. Unters. Lebensm.*, 1932, **63**, 267; ANALYST, 1932, **57**, 397). The ascorbic acid content of solutions of pure ascorbic acid, lemon juice and orange juice has been quantitatively recovered by the mercuric acetate precipitation. The reduction with hydrogen sulphide must be effected in a slightly acid medium, because otherwise, especially in alkaline solution, reducing sulphur compounds may be formed. It is important to mention that mercuric acetate solution removes many impurities; it also removes ergothioneine in acid medium. For the precipitation, a 20 per cent. solution of mercuric acetate in water is prepared and filtered after one day, as some hydrolysis takes place. To the solution to be tested (which must be slightly acid, excess of acid being removed by calcium carbonate and filtration) the mercuric acetate solution is added, drop by drop, in a graduated centrifuge-tube until the precipitation is finished. Care is taken to avoid a large excess of mercuric acetate. After centrifuging, the solution is treated with hydrogen sulphide, filtered, and left standing overnight, when the hydrogen sulphide is removed with nitrogen (controlled by lead acetate paper), and the titration is then carried out. *Example.*—To 20 ml. of a dilute orange juice solution (titration value 0·5 ml. indicator per ml. solution) 80 mgrms. of crystalline cysteine hydrochloride were added (4 mgrms. per ml.). This solution of ascorbic acid and cysteine decolorised, after 1 minute, about 0·9 ml. of indicator per ml. solution (the indicator being added, drop by drop, to the solution). From this solution 18 ml. (after calcium carbonate treatment) required 3 ml. of mercuric acetate solution, and the procedure given above was followed. Then 1 ml. solution required 0·43 ml. indicator, calculated $\frac{18}{21} \times 0{\cdot}5 = 0{\cdot}43$ ml. The sodium nitroprusside test was completely negative.

P. H. P.

Separation of Carotenes by Adsorption. H. H. Strain. (*J. Biol. Chem.*, 1934, **105**, 523–535.)—Separation of carotenes was found to be most successful by passing a solution of the carotene mixture over columns composed of a finely-divided adsorbent (Tswett columns). Magnesium oxide, prepared from the hydroxide and sold as Micron Brand magnesium oxide No. 2641 was found to be the most satisfactory adsorbent tried. This oxide exhibits a very high resolving power for different carotenes, so that each separated as a single and distinct zone on the column, and the carotenes were easily removable by elution with petroleum spirit containing ethanol; the magnesia may be used again after drying at 110–150° C. α- and β-carotenes, separated by this method, were identical with similar components separated from carrot-root and palm-oil by other methods, and with untreated carrot-root carotene of similar rotation. A small quantity of γ-carotene was also always isolated by adsorption on magnesium oxide, and smaller quantities of other coloured substances were found associated with it, but in no case was there any indication of a component of carrot-root carotene less readily adsorbed than α-carotene, by any of the adsorbents tried. Palm-oil, however, contained a small amount of a yellow carotenoid which was only slightly adsorbed on magnesium oxide. The preparation of the Tswett columns and the procedure with magnesium oxide as adsorbent are described in detail. Lead oxide, charcoal and siliceous earth with dichloromethane, and with petroleum spirit and dichloromethane, fibrous alumina, barium oxide, calcium oxide, calcium hydroxide, charcoal (norit), fullers' earth, lead hydroxide, basic lead carbonate, lead sulphide, mercuric chloride, and mercurous chloride, were all tried but were less successful than magnesium oxide as adsorbents. Magnesium oxide may also be used for separating carotenes from other pigments, such as lycopene and the chlorophylls and xanthophylls, and for the isolation of carotenes from natural products without any previous crystallisation. "Hydralo" was found excellent as an adsorbent for separating carotenes from lycopene, and from many naturally occurring waxes. D. G. H.

Stability of Carotene in Olive-Oil. R. G. Turner. (*J. Biol. Chem.*, 1934, **105**, 443–454.)—A 0·2 per cent. solution of carotene in olive-oil containing hydroquinone (0·1 per cent.) as stabiliser loses approximately one-half of its vitamin-*A* activity in a year. The action of light or of temperature up to 37·5° C. has little influence on this loss, but at 100° C. the destruction is hastened. Low temperatures retard the conversion of carotene to the achroo-form, and at 10° C. the loss of colour is no more rapid in absence than in presence of stabilisers. Quinhydrone is as effective as hydroquinone in preventing loss of colour. Without stabiliser, an olive-oil solution of carotene loses its colour completely in 6 to 9 months, and an ethyl-laurate solution in 3 to 4 months, at room temperature. When a stabiliser is present, both solutions tend to retain their red pigmentation at 6 to 7 red Lovibond units for 12 to 17 months, the vitamin activity having approximately one-half of its original value at this time. Apparently the loss of potency of carotene in highly concentrated solutions is not due solely to conversion of the active to the inactive form, slow precipitation until a saturation point is reached, being probably a contributory cause. T. H. P.

Determination of Carotene in Butter-Fat. H. M. Barnett. (*J. Biol. Chem.*, 1934, **105**, 259–267.)—The colours of solutions of carotene in petroleum spirit bear no constant relation to those of solutions in various edible oils. Butter-fat decolorised with activated carbon is useless as a solvent for carotene, which undergoes rapid decomposition in the fat. Carotene may, however, be determined spectro-photometrically if refined coconut-oil is used as a solvent and diluent. For the test experiments use was made of carotene purified by repeated crystallisation from hot petroleum spirit, 25 mgrms. of the product being dissolved in 50 grms. of the coconut-oil to make a stock solution. Curves are given showing the percentage transmission at wave-lengths varying from 455 to 500 $m\mu$ for concentrations of 0·5, 1·5 and 2·5 mgrms. of carotene per kgrm. of butter-fat in a 3-cm. cell. Application of these curves to determine the carotene in the fats of five butters shows good agreement between the concentrations indicated at ten different wave-lengths within the above region. Moreover, the method seems applicable also to dilute solutions of carotene in oils such as Wesson oil or oleomargarine, provided, of course, that carotene is the only pigment of consequence present.

In determining the carotene-content of butter-fat, it is suggested that the sample be diluted with refined coconut-oil so as to bring the carotene-content between 0·75 and 2 mgrms. per kilo., and that determinations be made at the various wave-lengths indicated, coconut-oil being used as a blank. An average of the results thus obtained should be more accurate than readings taken at only one or two wave-lengths. Moreover, by the use of a wider spectral region, any addition of foreign colouring matters may become apparent. The colorimetric method of determining carotene described by Palmer (*Carotinoids and Related Pigments*, Amer. Chem. Soc. Monograph Series, New York, 1932) gives inaccurate results, since the colour-intensity of carotene in oils is several times that in petroleum spirit. The values obtained by this method, when multiplied by 0·28, give results in good agreement with those of the above spectro-photometric method. The colorimetric method is hence useful if no spectro-photometer is available.

T. H. P.

Modified Spectrophotometric Method for the Assay of Carotene and Vitamin *A* in Butter. A. E. Gillam. (*Biochem. J.*, 1934, **28**, 79–83.)—Values for the carotene, xanthophyll and vitamin *A* contents of 70 English butters have been obtained spectrophotometrically. Mean values are recorded. It is shown that, on the average, the ratio of carotene to xanthophyll in butter is 14 : 1 by weight. It is further pointed out that if 94 per cent. of the light-absorption of butter-unsaponifiable matter at 455–460$m\mu$ is taken as being due to carotene, the results on individual samples are sufficiently close to those actually determined after removal of the xanthophyll to justify the approximation by the economy effected in time and material. The spectrophotometric method previously developed by Gillam, Heilbron, Morton, Bishop and Drummond (*Biochem. J.*, 1933, **27**, 878; ANALYST, 1933, **58**, 630) for the determination of carotene and vitamin *A* in butter has been improved for routine purposes. Full details of the modified method are given. To calculate the percentage of carotene in the butter, use in made of the fact that $E^{1\%}_{1\,cm.}$ 463$m\mu$ (in chloroform) = 1900 for pure carotene.

P. H. P.

New Colour Test for the Determination of Vitamin *A*. E. Rosenthal and J. Erdélyi. (*Biochem. J.*, 1934, **28**, 41–44.)—By a simple modification of the antimony trichloride reaction described by Carr and Price (*Biochem. J.*, 1926, **20**, 297) the authors have devised a reaction which is characteristic of vitamin *A*, and which allows its exact determination in cod-liver oil. When the oil containing vitamin *A* is heated together with catechol and antimony trichloride, both dissolved in chloroform, the blue colour first produced soon turns into a violet-red colour. The following reagents are necessary:—(i) Alcohol-free, absolute chloroform. (ii) A freshly-prepared 0·5 per cent. solution of catechol in chloroform. (iii) A cold saturated solution of antimony trichloride in chloroform. The specimen of oil to be tested is first diluted with chloroform. To 1 ml. of this solution 1 ml. of the catechol solution and 3 ml. of the antimony trichloride solution are added. The test-tube containing the mixture is immediately transferred to a water-bath at 60° C. for 1 to 2 minutes. The blue colour first produced changes during this heating into an intense violet-red hue. In the cold this colour is not produced, as the change then takes the same course as without catechol. Subsequent heating of the solution which has undergone the change in the cold does not lead to the production of the violet-red colour; therefore, heating must take place immediately after the mixing of the reagents. For quantitative determinations, the solution, immediately after it has turned violet-red, is compared in a colorimeter with a 0·01 per cent. solution of potassium permanganate. From 0·1 to 0·5 ml. of cod-liver oil should be used, diluted with chloroform to 1 ml. Spectroscopic examination of the red fluid shows four characteristic absorption bands: (i) A broad band at the boundary of green and yellow, having indistinct limits; peak intensity at $552 m\mu$; (ii) a narrower distinct band between green and blue; peak intensity at $476 m\mu$; (iii) a dim band in the blue; and (iv) a dim band in the violet. Vitamin *A* solutions inactivated by irradiation do not give the reaction. The following carotenoids which were examined do not give the reaction: Carotene, lycopin, zeaxanthin, capsanthin and physalin. The same reaction carried out with ergosterol shows the colour change in an inverse succession, the solution first becoming pink and changing slowly to blue. The reaction with catechol, as described, is an advance in two respects: (i) it makes possible differentiation of vitamin *A* from carotenoid substances; (ii) the violet-red colour, similar to that of a dilute solution of potassium permanganate, is more stable than the blue colour obtained according to the Carr and Price method. P. H. P.

Some Factors which affect the Assay of Vitamin *A* by the Spectrographic Method. R. J. MacWalter. (*Biochem. J.*, 1934, **28**, 472–475.)—Measurements of vitamin *A*-content, on the basis of absorption at $328 m\mu$, involve the assumption that irrelevant absorption at this wave-length bears a constant relation to the relevant absorption for all oils, or is negligible in comparison with it. Aeration experiments show that this is not the case, and suggest that the ageing of an oil by oxidation may increase the irrelevant and decrease the relevant absorption. The measurements should be made on the unsaponifiable fraction in order to avoid errors arising from previous oxidation. The vitamin-content, as measured by the absorption at $328 m\mu$, is regarded of value only with oils having a potency exceeding 10 to 20 blue units (C.P.). For less potent oils, the "non-vitamin *A*" absorption is a considerable fraction of the total absorption. S. G. S.

The Formaldehyde-Azo-Test for Vitamin B_1. H. W. Kennersley and R. A. Peters. (*Biochem. J.*, 1934, **28**, 667–670.)—The test for vitamin B_1, by means of diazotised sulphanilic acid (the Pauly reaction), has been found to require a definite p_H value, and also to be more stable in the presence of formaldehyde. The reagent is prepared by dissolving 5·76 grms. of sodium bicarbonate in 100 ml. of water and adding 100 ml. of *N* sodium hydroxide solution. For the test, 0·5 ml. of diazotised sulphanilic acid [To 1·5 ml. of sulphanilic acid solution (4·5 grms. + 45 ml. of 37 per cent. hydrochloric acid (sp.gr. = 1·19) dissolved in 500 ml. of water), 1·5 ml. of sodium nitrite solution (25 grms. of 90 per cent. sodium nitrite in 500 ml. of water) is added and the mixture left in ice for 5 minutes. Six ml. of sodium nitrite solution are then added, and the mixture is again placed in ice for 5 minutes, after which it is diluted to 50 ml. and kept in ice 15 minutes before use. (See also Koessler and Hanke, *J. Biol. Chem.*, 1919, **39**, 505.)] is added to 1·25 ml. of the reagent in a small test-tube. After one minute, 1 drop (0·3 ml.) of 40 per cent. formaldehyde is added, and then the vitamin B_1 in 0·1–0·3 ml. of solution of acidity greater than p_H 4·0. A pink colour develops slowly, and increases in intensity for 30 to 60 minutes. After this time it is almost constant, although the pink becomes more pronounced up to 24 hours, owing to the fading of the yellow. Standards may be made with different concentrations of the vitamin, from 2 to 7 pigeon-doses, and kept for 14 days. The limit of sensitivity is 1 vitamin B_1 unit (1 pigeon-dose or 1·5–2·0γ of crystalline vitamin). With 1 unit, the colour is ill-defined. Even in the purest specimen yet obtained the colour is tinged with yellow. The colour from 10γ approximates to that from a mixture of Sørensen's acid and alkaline phosphates (2 + 8) of p_H 5·0 at 15° C., containing in 103 ml., 100 ml. of phosphate mixture and 3 ml. of 0·02 per cent. phenol red. A simple comparator is preferred to a colorimeter, but the use of the tintometer has not been properly explored. The test can be used as a preliminary one for extracts of seeds, roots, etc., and also for fractionation of the vitamin, as it agrees closely with the bird-test. S. G. S.

Bacteriological

Individual Resistance of Micro-organisms, especially Yeasts, to Ultra-violet Rays. J. Beauverie. (*Compt. rend.*, 1934, **198**, 2017–2019.)—The value of cellophane in experiments on the effect of ultra-violet rays on micro-organisms is emphasised. This material is traversed by rays of wave-length down to 250$m\mu$, and thus transmits abiotic rays. Moreover, preparations made on it may be observed directly under the microscope, even with an immersion lens. In the experiments described, yeast from a young culture on wort-gelatin was mixed with water to a thin emulsion, portions of which were spread on sheets of cellophane. These were examined under the microscope to ensure that only single layers of cells were present. One preparation was kept in a moist atmosphere as a control, and the others were exposed for 30 seconds, 3 minutes or 5 minutes, at a distance of 30 cm., to the radiation of a 400-watt mercury vapour lamp (15,000 volts). The first effect of the exposure is to inhibit the multiplying power of the cells. This is followed by alteration in their structure, which shows itself in more or less deformed vacuoles and increasingly granulated cytoplasm, and is, to some extent, reversible, although it may continue until the cell is killed.

T. H. P.

***Byssochlamys Fulva* and its Effect on the Tissues of Processed Fruit. M. Olliver and T. Rendle.** (*J. Soc. Chem. Ind.*, 1934, **53**, 166–172T.)—An unusual feature observed during an investigation on the softening of sound fruit, which had been processed under normal conditions and stored for several weeks, was disintegration without obvious gas-production, abnormal odour or flavour, or colour-change, the general effect being merely that of over-processing; this was found to be due to a new species of fungus, *Byssochlamys fulva* (*cf.* Olliver and Smith, *J. Botany*, 1933, **72**, 196). The most striking characteristics of young cultures of this fungus, which resists normal processing conditions and grows well in a reduced supply of oxygen, are very long tangled chains of ovate to elongate conidia which arise from sterigmata with swollen bases. Ten-day cultures produce masses of asci, which appear as spheres in the mycelial felt and develop eight ascospores each, and these are very resistant to physical and chemical changes; there is no peridium or hyphal web. *B. fulva* is cultivated best on a medium prepared by steaming 100 grms. of potato mash with 800 ml. of tap water for 30 minutes; the filtrate from this mixture is diluted with an equal volume of water, and to this are added, agar, 1·5 per cent.; sucrose, 10·0; magnesium sulphate, 0·1; dipotassium hydrogen phosphate, 0·1; sodium chloride, 0·1; ammonium sulphate, 0·2; and calcium carbonate, 0·2 per cent. The medium is autoclaved for 30 minutes at 15 lbs., and is then filtered and sterilised. The optimum growth-temperatures are between 30 and 37° C., and the mycelium may be floccose, filmy, leathery or waxy according to the conditions, and is usually filmy or waxy on fruit, although it bears no relationship in quantity to the degree of disintegration produced. *B. fulva* also grows on Czapek-Dox agar, on Henrici's peptone-sucrose, and (without producing liquefaction) on gelatin; it inverts and degrades sucrose, the maximum concentration tolerated being 60 to 65 per cent. Experiments indicate that the softening action on fruit is due to destruction of the cementing pectinous substances rather than of the cellulose, and this is accelerated by addition of inorganic salts and, particularly, of 1 per cent. of peptone; this may explain the wide variations in effect observed in practice and with different fruits (*cf.* Raistrick and Smith, *Biochem. J.*, 1933, **27**, 1814). Results are erratic with fruit juices, probably on account of submergence of the spores, and, although *B. fulva* is not parasitic, so far as fruit on the plant is concerned, it is capable of rapid growth on damaged surfaces. The source of *B. fulva* has now been traced to the fields and orchards, where strawberries, damsons and plums seem most liable to attack (37, 50 and 71 per cent., respectively, of those examined were infected). It is suggested that *B. fulva* is present on fruit only by reason of atmospheric distribution of the conidia or asci, or by direct contamination from the soil, and that processed fruit provides the ideal medium for its growth; it has been found in 16 different districts in England, but is apparently unknown abroad. Cold storage at 10° to 20° F. for several months, and treatment with ammonia (2·5 ml. per litre) and with acetaldehyde (1 part in 200) inhibits growth without killing; mature ascospores in certain fruit syrups survived temperatures of 86° to 88° C. for 30 minutes, and exposure to live steam for 3·5 minutes was required before the fungus was killed. The fungus tolerates concentrations of sulphur dioxide (in the presence of sucrose and peptone) up to 450 parts per million, and is comparatively little affected by changes in p_H value of 2·0 to 7·0 (optimum growth at 3·0) and, in the case of old cultures, by immersion in 100 per cent. alcohol. J. G.

Toxicological and Forensic

Sericite in Foundry Dust. C. S. Hurlbut and D. S. Beyer. (*J. Ind. Hyg.*, 1934, 169–176.)—A study of the dusts of two foundries carrying out similar operations showed that the dust in one was extremely high in sericite, whilst the other had only a moderate amount. This difference was traced to the moulding sands used. A high incidence of silicosis claims occurred in the foundry in which the dust was high in sericite, in spite of lower dust-counts and more favourable employment conditions in that foundry. No silicosis claims were made in the foundry having little sericite. The findings in these respects were in harmony with those of Jones. A sericite-rich sand may contribute a large percentage of sericite particles to the respirable dust in a foundry, even though this sand is only a small portion of the total. Sericite particles, because of their shape, will remain suspended in the air longer than quartz particles of the same size. Further studies should be made to determine the sericite-content of foundry sands, particularly those used where silicosis claims have arisen. Meanwhile, preference may well be given to the use of foundry sands having little or no sericite. An experiment confirmed the previous deduction, and showed that the original high percentage of sericite, relative to quartz and other constituents, increased with time. After 75 minutes of settling in still air, nearly 100 per cent. of the material remaining in suspension was sericite.

Agricultural

Determination of Aluminium in Pasture-Grasses, etc. F. B. Shorland. (*Trans. Roy. Soc. New Zealand*, 1934, **64**, 35–49.)—The method employed was essentially that used by Lampitt and Sylvester for the determination of aluminium in foodstuffs (ANALYST, 1932, **57**, 418), involving colorimetric determination of the red aluminium lake of aurintricarboxylic acid with the aid of the Lovibond tintometer; it was found to be accurate to within about 5 per cent. Careful cleaning of the sample grasses prior to analysis was found to be necessary in order to remove dust and soil particles, which frequently contain appreciable amounts of aluminium, and lack of attention to this detail is considered to have resulted in previous investigators over-estimating the aluminium content of these materials. The method of cleaning adopted was thoroughly to brush the selected material to remove loosely adhering matter; a weighed sample was then washed in several successive changes of distilled water until the washings showed no appreciable amount of suspended matter. The destruction of the organic matter, either by ashing or by wet oxidation with nitric and sulphuric acids, is stated to leave from 35 to 65 per cent. of the total alumina in the insoluble residue; no details for the recovery of this part of the alumina are given. The distribution of alumina in bamboo, pampas-grass, toetoe (*Arundo conspicua*), rye grass, red and white clovers was studied, the amounts of alumina found varying from 0·0025 per cent. in bamboo stems to 0·114 per cent. in rye-grass roots. The alumina was shown to be concentrated chiefly in the roots, but the leaves contained more than the stems. The figures obtained on carefully cleaned pastures show that, in general, the alumina-content is below 0·025 per cent., and values quoted in excess of this are considered to indicate contamination of the sample by dust, etc. S. G. C.

Determination of Naphthalene in Insecticides. W. L. Miller. (*J. Assoc. Off. Agric. Chem.*, **1934**, **17**, **308–313**.)—The following methods have a higher degree of accuracy than existing procedures and, with the exception of that for louse powder (which is recommended as a check or for use in the presence of volatile solvents), are considerably shorter:—*In Mineral Oils.*—Cresols, phenols or alkaloidal bases are removed by extraction in succession with 10 per cent. sodium hydroxide solution, dilute acid and water, and 10 ml. of the residual sample are extracted twice with 20 ml. of a mixture of 90 ml. of acetone and 10 ml. of water. The extracts are transferred to the heavier of two Babcock cream bottles which balance to within 3 grms., 10 ml. of water are added, the mixture is shaken, and 3 minutes later the oil which rises is returned to the separating funnel; the extraction process is then repeated, this extract being transferred to the other bottle. Both bottles are then centrifuged at 1200 r.p.m. for 10 minutes, the top layers are removed, and the combined residues are diluted to 100 ml. with the acetone solution. Of this, 50 ml. are pipetted, with stirring, into 250 ml. of a saturated solution of picric acid, and after 5 minutes the precipitate is collected on a Gooch crucible containing filter paper and a thick layer of asbestos, and washed with a 0·2 per cent. solution of picric acid. The contents of the crucible are then boiled for 5 minutes with 200 ml. of water and an excess of 0·1 *N* sodium hydroxide solution, the mixture being then cooled and titrated with 0·1 *N* hydrochloric acid to phenolphthalein (x ml.). If 0·05 ml. is deducted for the picric acid retained on the filter and a further 0·05 ml. for each 20 ml. of alkali required, then 0·012806x gives the naphthalene-content.

In Low-boiling Solvents.—A quantity of sample containing not more than 5 grms. of naphthalene and 7 grms. of *p*-dichlorobenzene is diluted to 100 ml. with chloroform, and 10 ml. of the mixture are stirred with 1 grm. of picric acid and 10 ml. of chloroform. The solvent is removed on the water-bath below its b.pt., and the residue is dissolved in 15 ml. of warm alcohol to which 100 ml. of water are added. The mixture is cooled and filtered, and the residue is titrated as described above.

In Wood Chips and Essential Oils.—A sample containing not more than 1 grm. of naphthalene is extracted for 10 minutes with 40 and 20 ml. of hot alcohol in succession, and half of the combined and diluted extracts (50 ml.) is mixed with

200 ml. of a cold saturated solution of picric acid, the mixture being then filtered and titrated as described above.

In the Presence of p-*Dichlorobenzene, Camphor and Inorganic Fillers.*—An aliquot portion of a solution of the sample in acetic acid (equivalent to 0·10 to 0·15 grm. of naphthalene) is added to a mixture of 80 ml. of water, 40 ml. of concentrated sulphuric acid and sufficient acetic acid to provide a total of 70 ml. of this substance. The mixture is warmed to 70° C., and 0·5 N potassium permanganate solution is added until the rose colour no longer rapidly fades to orange. The temperature is then raised to 90° to 91° C., and the addition is continued at such a rate that the two colours just merge, the reading (x ml.) being taken as soon as the rose colour persists for 6 seconds; then the percentage of naphthalene $= 0{\cdot}5 \times 0{\cdot}7115x/(\text{weight of sample})$. The reaction is controlled oxidation to phthalic acid, and camphor interferes, since it also is oxidised under these conditions.

Louse Powders, etc.—A 500-ml. Kjeldahl flask is provided with an inlet connected with a steam-generator, and reaching to the bottom, and an outlet of 7 mm. tubing projecting a short distance into the flask, and connected with a condenser composed of 20-mm. tubing. This delivers into a cooled 1000-ml. Erlenmeyer flask provided with an air-vent and containing sufficient water to cover the end of the condenser. The sample (equivalent to at least 2 grms. of naphthalene) is weighed into the flask, 100 ml. of water and a little sodium hydroxide solution are added, and the naphthalene is removed by slow steam-distillation for 1 hour. The distillate and rinsings are filtered after acidification with sulphuric acid, the naphthalene being then washed with a little water and dissolved in at least 50 ml. of hot acetic acid. An aliquot portion of the resulting solution is treated as described in the preceding method. One per cent. of essential oil (which, however, is rarely present) gives an error in the direct titration of 0·5 to 1·5 per cent. Satisfactory results were obtained for 20 samples of the above types containing 1·91 to 73·42 per cent. of naphthalene; refined and commercial naphthalenes gave values of 100·08 and 99·47 per cent., respectively. J. G.

Colorimetric Method for the Determination of Rotenone. C. R. Gross and C. M. Smith. (*J. Assoc. Off. Agric. Chem.*, 1934, 17, 336–339.)—Since the Jones gravimetric method (*Ind. Eng. Chem., Anal. Ed.*, 1933, 5, 23) is inapplicable to small quantities, and the Durham colour reaction (*id.*, 1933, 5, 75) is not sufficiently permanent for quantitative work, the following procedure is suggested: —A solution of the sample in acetone (other solvents, including methyl ethyl ketone, are unsatisfactory), corresponding with 0·05 to 0·3 mgrm. of rotenone per ml., is prepared, and 2 ml. are mixed with 2 ml. of a fresh, clear and colourless 10 per cent. solution of potassium hydroxide in 95 per cent. ethyl alcohol in a test-tube, which is then immersed in a bath at 20° C. for exactly 2 minutes. Six ml. of a mixture containing equal volumes of nitric acid and a 0·025 per cent. solution of sodium nitrite are then added, and the tube is quickly stoppered and cooled to 20° C. by immersion in the bath for at least 30 seconds; the resulting red colour is matched after 15 minutes, but before 50 minutes, against that produced from a standard at the same time and under the same conditions. After several hours a vigorous reaction occurs which may cause the contents of the tube to boil over. Dihydrorotenone and deguelin give the reaction, but toxicarol, tephrosin, *iso*-tephrosin, nicotine, pyrethrum extract, or the primary decomposition-products of rotenone and deguelin (dehydrorotenone, rotenone and dehydrodeguelin) do not interfere. High results (by 50 to 100 per cent. compared with the gravimetric method) obtained with derris or tuba roots were attributed mainly to deguelin, although the possibility of the presence of other unidentified constituents also exists. A mixture of 1 per cent. of rotenone in diatomaceous earth gave six results ranging from 0·94 to 0·98 per cent., and 7 samples of commercial rotenone containing 86 per cent. and 1 containing 65 per cent. of rotenone (according to the polarimetric and gravimetric methods) were shown to contain 85 to 90 and 82 per cent., respectively. Fruit or leaves should be washed with a jet of acetone. Analyses made several weeks after spraying showed the presence of 7 to 30 mgrms. per fruit and 1 to 5 mgrms. per leaf for rotenone, and rather higher results for a derris spray. J. G.

Organic Analysis

Oxidation by means of Organic Per-Acids. J. Böeseken. (*Chem. Weekblad*, 1934, 31, 166–170.)—The literature of the applications of oxidation by organic per-acids to investigations in organic chemistry is reviewed critically, and numerous examples are cited. Per-acetic acid is most commonly employed, and is usually prepared by the action of strong hydrogen peroxide on acetic anhydride in the presence of a little concentrated sulphuric acid, which is added as a catalyst towards the end of the reaction; if the proportion of hydrogen peroxide is not allowed to exceed 80 per cent., and the temperature is kept below that at which the flask can be held in the hand, a yield of 30 to 50 per cent., free from acetyl peroxide is obtained by subsequent distillation (*cf.* W. C. Smit, *Rec. Trav. Chim. Pays-Bas*, 1930, 49, 685). Strong solutions of per-acetic acid in glacial acetic acid are not spontaneously explosive so long as catalytic impurities are absent and the temperature does not exceed 30° to 40° C. On one occasion a violent explosion was traced to the presence of a little acetyl peroxide in the distillation flask, and the potassium iodide and starch test should therefore be applied to ensure its absence; acetyl peroxide hydrolyses slowly, with the formation of acetic and per-acetic acids. On the other hand, per-benzoic acid (m.pt. 41° to 43° C.), which is best prepared by the action of sodium ethoxide on dibenzoyl peroxide (*cf.* Baeyer and Villiger, *Ber.*, 1900, 33, 1569), may be handled safely if dissolved in ether or in chloroform, although such solutions are less suitable for storage than solutions of per-acetic acid in glacial acetic acid. J. G.

Identification of Amino Acids by means of 3 : 5-Dinitro-Benzoyl Chloride. B. C. Saunders. (*Biochem. J.*, 1934, 28, 580–586.)—3 : 5-Dinitrobenzoyl chloride is recommended as a reagent for the rapid identification of many amino-acids. In alkaline solution the condensation is almost instantaneous, giving a good yield of crystalline derivative. The normal proportions are 1 mol. of amino acid to 1 mol. of the acid chloride in the presence of 2 mols. of sodium hydroxide, but different acids require slightly different treatments. Some of the derivatives are insoluble in alkali, others require precipitation by dilute acetic or hydrochloric acid. The acidic amino acids are less reactive to this reagent, and this has been made the basis of a method of separating glycine and several other amino acids from aspartic acid. Glycine can be separated from glutamic acid by this method, for, although both give derivatives, that from glycine is formed preferentially. Tyrosine does not react in alkaline solution, neither does oxidised glutathione. Thiolacetic acid gives an S-3 : 5-dinitrobenzoyl thiolacetic acid, and although cysteine gives an S-derivative, it cannot be used for identification. The method is an improvement on the pyridine one of Wertheim (*J. Amer. Chem. Soc.*, 1929, **51**, 3661), as no fusing is necessary. S. G. S.

Condensations of Furan Compounds. III. Condensation Products of Furfural with Acetone in Acid and Alkaline Media, and a New Method of Determining Small Quantities of Furfural. W. W. Tschelinzeff and E. K. Nikitin. (*Bull. Soc. Chim.*, 1934, **1**, 184–189.)—In either an acid or an alkaline medium, furfural condenses with acetone, giving difurylidene-acetone or, if the acetone is in excess, furylidene-acetone. Under the action of sulphuric acid, these products condense, giving, for the former a reddish-violet, and for the latter an orange-red compound. By means of the first of these, acetone may be determined (*ibid.*, 1932, **51**, 875), and the second is now used for determining furfural.

To detect furfural, a glass rod, moistened with a drop of acetone containing 1 mgrm. of concentrated hydrochloric acid, is placed in the liquid to be tested or in the vapour therefrom; a bright orange-red colour indicates furfural. This reaction is shown in presence of other substances, but aliphatic aldehydes react with acetone before the furfural does, so that excess of acetone must be ensured. As little as 0·001 per cent. of furfural in solution is detectable in this way.

For the determination, 1 ml. of the solution, containing not more than about 0·1 per cent. of furfural, is mixed with 0·1 ml. of acetone (purified by formation of the bisulphite compound, hydrolysis and distillation, this series of operations being carried out three times, and the final product dried over anhydrous sodium sulphate) and 5 ml. of 50 per cent. sulphuric acid. The mixture is heated in a water-bath at 50° C. for 30 minutes, and the colour developed compared in a colorimeter with that obtained similarly from 1 ml. of 0·1 per cent. furfural solution. The intensity of the coloration is accurately proportional to the concentration of the furfural. The condensation of the furfural and acetone may be effected by means of sodium hydroxide, at 20° C., the liquid being acidified prior to the colour comparison. In this case the intensity of the resulting coloration is proportional to the square of the concentration of the furfural, the condensation in the alkaline medium evidently following a course different from that in the acid medium. T. H. P.

Observations on the Action of Chlorine on Lignified Tissues. F. M. Wood. (*Biochem. J.*, 1934, **28**, 52–61.)—During an investigation of the origin of a pink colour produced in lignified tissues when the chloramine reaction is employed, differential tests for coniferin and vanillin were made, since it was thought possible that the colour might be due to a compound of vanillin or coniferin, or their derivatives, with chlorine. Other possibilities were that it might be due to a compound of lignin with chlorine or to the nature of the lignin present. Experimental work is described in which it is shown that the colour is not due to lignone chloride or to the products of chlorination removable by sodium sulphite, that it is closely associated with the presence of iodine and also of lignin, but that the nature of the lignin itself is not concerned, so that the latter association is either very loose or the substance is "encrusted" on the lignin. It is shown that vanillin is present when the colour is produced, and that there is more vanillin in older than younger tissues, in autumn than spring wood, in cortical than in stelar sclerenchyma, and that it is naturally present in the cell-wall. Hemicelluloses and coniferyl alcohol are not responsible for the observed effect. Under conditions similar to those used with plant sections experiments were made with vanillin, chlorovanillin, vanillic acid, vanillic acid treated with chlorine, and amines or chloramines, in which filter-paper, "Tarantulle" and wood-pulp were used upon which to "encrust" the compounds concerned. Indications were obtained that a vanillal derivative was formed which reacted with iodine to produce a substance coloured similarly to that obtained in plant tissues. The conclusion drawn is that vanillin, in loose association with some form of lignocellulose, is acted upon by chlorine, producing a chlorovanillin, which with the chloramines produced from protein within the cell, forms a vanillal derivative forming a pink substance in the presence of iodine. Should the chlorine not affect the vanillin to any marked degree, probably vanillin itself may react with the chloramines from the cell-contents and still produce the colour. It is possible that both series of reactions take place simultaneously. The possibility that vanillin is an excretory product, produced when the function of the tissues concerned has become chiefly that of mechanical support, is discussed. This theory is upheld by the fact that vanillin predominates in older tissues and in autumn wood. P. H. P.

Tetrachlorophthalimide as a Reagent in Qualitative Organic Analysis. C. F. H. Allen and R. V. V. Nichols. (*J. Amer. Chem. Soc.*, 1934, **56**, 1409.)—The potassium derivative of tetrachlorophthalimide reacts with many halogen compounds to give substituted tetrachlorophthalimides, which are useful for purposes of identification. A list of the melting-points of some 24 derivatives which have been prepared is given in the paper, and an improved method of preparation of the reagent is described. S. G. C.

Inorganic Analysis

Cadmium Sulphate as a Basis for Acidimetry. S. E. Q. Ashley and G. A. Hulett. (*J. Amer. Chem. Soc.*, **1934**, **56**, 1275–1278.)—The clear, well-developed crystals of $3CdSO_4.8H_2O$, which are obtained by crystallisation of cadmium sulphate from aqueous solutions, are claimed to be a satisfactory standard material for standardisation purposes. A weighed crystal, or quantity of crystals, is dissolved in water, and the solution is electrolysed over a mercury cathode for a time sufficient to cause the deposition of the whole of the cadmium. The solution, which then contains the stoichiometric amount of free sulphuric acid, is removed from the electrolytic cell (which is finally washed out with water), and is used for the standardisation of alkali in the usual way. The results obtained with alkali solution standardised independently had a mean deviation from the theoretical of 3·5 parts per 10,000. S. G. C.

Selenium as Indicator in the Bromate Titration of Arsenic. L. Szebellédy and K. Schick. (*Z. anal. Chem.*, 1934, **97**, 186–191.)—Colloidal selenium can be used as a reversible oxidation-reduction indicator. Under the conditions given below, which must be carefully adhered to, it gives good results in the bromate titration of arsenious acid. The arsenite solution is treated with 5 grms. of sodium bromide, and diluted to 35 ml. Strong hydrochloric acid (25 ml.) is added, and the solution is warmed to 55° or 60° C. After addition of 1 ml. of a molar solution of selenious acid (which produces a dark red colour) the solution is titrated with 0·1 *N* bromate solution, added drop by drop, until the last of the pink cloudiness is removed with a single drop of bromate solution.
W. R. S.

Volumetric Determination of Tin with Potassium Iodate. J. B. Ramsey and J. G. Blann. (*J. Amer. Chem. Soc.*, 1934, **56**, 815–818.)—The reduction of tin to the stannous condition is effected by precipitation on zinc and solution of the spongy tin in hydrochloric acid in an atmosphere of carbon dioxide, 0·1 grm. of nickel or cobalt chloride being added to hasten solution of the sponge. The solution is then cooled in water, while carbon dioxide is passed through the flask, and diluted with 100 ml. of 0·2 *N* sodium bicarbonate solution (freed from air by boiling, and cooled in a current of carbon dioxide). The acidity of the resulting solution should be approximately normal. It is titrated under carbon dioxide with potassium iodate solution until a faint yellow colour proves liberation of iodine. The sides of the flask are at once washed down, and the excess of iodine is determined with thiosulphate and starch solution. The results by this method are claimed to be more accurate than those obtained by the usual iodine titration, which the authors show to give slightly low results. W. R. S.

Butylphenylarsonic Acid as a Reagent for the Gravimetric Determination of Iron. K. A. Craig and G. C. Chandlee. (*J. Amer. Chem. Soc.*, 1934, **56**, 1278–1279.)—The ferric iron solution (200 ml.), which may contain hydrochloric, nitric or sulphuric acid, is adjusted in acidity to 0·4 *N*, heated nearly to boiling, and 0·75 grm. of the reagent, dissolved in 100 ml. of hot water (80° to 90° C.), is added with stirring, yielding a white flocculent precipitate of the iron compound. The liquid is kept hot for 20 to 30 minutes and allowed to cool; the precipitate is filtered off, washed first with warm 0·02 *N* hydrochloric acid, and then with warm water, ashed, and ignited to ferric oxide. The accuracy was found to be within 4·5 parts per 1000 in tests with solutions of iron salts alone and in the presence of 0·1 to 0·2 grm. of dissolved nickel, cobalt, manganese, copper or cadmium oxide, and also 0·05 to 0·1 grm. of the dissolved oxides of potassium, aluminium, magnesium, calcium, beryllium, vanadium, lanthanum, erbium, and neodymium. In the presence of chromium as dichromate, reprecipitation was necessary after dissolving the first formed precipitate in acid, whilst with thallium present, the precipitate required to be washed with a saturated solution of the reagent in

1 per cent. hydrochloric acid, in order to remove hydrolysed thallium salt. The precipitation is prevented by substances which form complex compounds with iron—for example, fluoride or tartrate. The following interfere: Zirconium, tin, thorium, uranium, and cerium. Satisfactory results were obtained in the direct determination of iron in Monel metal and German silver. S. G. C.

Separation of Iron, Aluminium, and Chromium from Bivalent Metals by means of Ammonium Benzoate. I. M. Kolthoff, V. A. Stenger, and B. Moskovitz. (*J. Amer. Chem. Soc.*, 1934, **56**, 812–815.)—The reagent is a solution of 100 grms. of ammonium benzoate in 1 litre of water. The chloride solution of the metals (100 ml.), containing iron as ferric salt, is cautiously neutralised with dilute ammonia until the precipitate re-dissolves very slowly, and treated with 1 ml. of glacial acetic acid and ammonium chloride, if necessary, to the total amount of 1 grm.; a measured volume of the reagent (20 ml. per 0·065 grm. Al or 0·125 grm. Fe or Cr) is slowly stirred in. The liquid is stirred and heated to gentle boiling (5 minutes if chromium is absent, 20 if it predominates). The precipitate is collected and washed with a solution containing 10 grms. of ammonium benzoate and 20 ml. of glacial acetic acid per litre. For exact work the filtrate and washings should be evaporated to about 50 ml. for the recovery of any non-precipitated iron or chromium. The co-precipitation of the bivalent metals is much less pronounced than in the ammonia method, a single precipitation being usually sufficient in ordinary work. Phosphoric acid is partly co-precipitated.

W. R. S.

Determination of Zinc in Steel. H. A. Bright. (*Bureau of Stds. J. Research*, 1934, **12**, 383–389.)—Three methods have been investigated. (*a*) *Ammonia Precipitation Method.*—The solution of a 5-grm. sample in dilute sulphuric acid, oxidised with ammonium persulphate, is poured slowly, with stirring, into a considerable excess of dilute ammonia solution containing about 4 grms. of dissolved ammonium sulphate, and the solution, containing the zinc, is filtered, the precipitate being washed with ammoniacal ammonium sulphate solution (2 per cent.). The filtrate is evaporated to about 150 ml., neutralised to methyl orange indicator with 1 : 1 sulphuric acid, and 7·5 ml. of this acid are added in excess. Any copper or molybdenum present is precipitated from the solution with hydrogen sulphide, and the sulphides are filtered off and washed. The filtrate is boiled to expel hydrogen sulphide, and cooled; the solution is neutralised with ammonia, and sulphuric acid is added to give an acidity of 0·01 *N*. The zinc is then precipitated with hydrogen sulphide in the usual way, and the precipitate is finally ignited to zinc oxide. The method gave good results with 0·005 to 0·30 per cent. of zinc. (*b*) *Ether Extraction Method.*—The iron in a solution of 25 grms. of the steel is removed by the usual method of extraction with ether; the hydrochloric acid in the aqueous solution is removed by evaporation with sulphuric acid; the residue, after dilution, is poured into ammonia, and the determination is completed as in (*a*). This method was found to be the most satisfactory for amounts of zinc of the order of 0·001 per cent. (*c*) *Direct Precipitation with Hydrogen Sulphide.*—A 15-grm. sample is dissolved, so far as possible, in 96 ml. of 1 : 5 sulphuric acid, and the solution is filtered. The filtrate is diluted to 450 ml., and 5 grms. of ammonium sulphate and 60 ml. of citrate buffer solution (20 grms. of citric acid and 450 grms. of sodium citrate dissolved in 1 litre) are added, yielding a solution of p_H 2·5. The solution is saturated with hydrogen sulphide and kept overnight. The precipitate is filtered off, and dissolved in hot 1 : 9 sulphuric acid; the solution is boiled to remove hydrogen sulphide, and any copper, etc., is precipitated with hydrogen sulphide after adjustment of the acidity to about 2·5 per cent. of sulphuric acid. The precipitate is filtered off, and the zinc in the filtrate is determined as in (*a*). The method gave satisfactory results when 0·003 per cent. or more of zinc was present. The three methods were tested on solutions of various steels, in some cases known to be spectroscopically free from zinc, to which known amounts of zinc had been added. The results of analyses of 4 representative materials showed that the zinc-content of steels and irons is very small—of the order of less than 0·0005 per cent. S. G. C.

Gravimetric Determination of Thallium as Cobaltinitrite. S. Nisihuku (*J. Soc. Chem. Ind. Japan, English Abstr.*, 1934, **37**, 180B.)—Thallium may be precipitated as thallium cobaltinitrite $Tl_3Co(NO_2)_6$ by addition to the solution of sufficient of cobaltinitrite reagent [a mixture of equal volumes of a solution of (*a*) 28·6 grms. of cobalt nitrate and 50 ml. of 50 per cent. formic acid in 500 ml., and of (*b*) 180 grms. of sodium nitrite in 500 ml.], both the test solution and the reagent being previously warmed to about 40° C. The compound, which is formed as a scarlet crystalline precipitate containing 64·67 per cent. of thallium, is filtered off after 1 hour, washed with cold water, and dried at 120° C. The method is stated to have been applied to the determination of thallium and its separation from other metals, but no further details are given. S. G. C.

Determination of Iodide by Photometric Titration. S. Hirano. (*J. Soc. Chem. Ind. Japan, English Abstr.*, 1934, **37**, 177–178B.)—When an acid solution of an iodide is titrated with iodate solution, the reaction (1) occurs so long as iodide is present, the result being that the solution becomes progressively darker in colour owing to the iodine being liberated. On continuing the titration, the

$$(1)\quad IO_3^- + 5I^- + 6H^+ = 3I_2 + 3H_2O.$$
$$(2)\quad IO_3^- + 2I_2 + 6H^+ = 5I^- + 3H_2O$$

reaction (2) occurs, and the colour becomes progressively paler. Hence, measurement of the colour tone of the solution affords a means of determining the iodide. The author measured by means of a photo-electric cell the light transmitted through the solution during the titration of 0·01 *N* potassium iodide solution with 0·01 *N* potassium iodate solution, and found a sharp minimum corresponding with the end-point of reaction (1); it was concluded that the method is suitable for determining small amounts of iodide. S. G. C.

Microchemical

Detection of Sucrose in Lactose. M. Wagenaar. (*Pharm. Weekblad*, 1934, **71**, 281–284.)—The test depends on the fact (*id.*, 1933, **70**, 1030) that a solution of α-naphthol in glycerin gives, in the presence of sulphuric acid, a blue-violet or an orange condensation-colour in the presence of a ketose or aldose group, respectively. A suspension of 5 mgrms. of the sample in a drop of reagent is therefore mixed on a microscope slide, by means of a platinum wire, with a drop of concentrated sulphuric acid; a blue-violet colour after 10 minutes, particularly at the edge of the drop, indicates the presence of a ketose compound. If the result at this stage is negative, it is advisable to hold the slide over a boiling water-bath for about 30 seconds, and to compare the resulting colour with that obtained with a specimen of pure lactose after similar treatment. The reaction is specific for fructose or sucrose, and will detect 1 per cent. or more of the latter; it may be applied to the residue after evaporation of the solution obtained by extracting the sample (according to the Dutch Pharmacopoeia) with dilute alcohol, which dissolves the sucrose in preference to the lactose. J. G.

Micro-titrimetric Determination of Nicotine in Tobacco. J. Bodnár and v. L. Nagy. (*Z. Unters. Lebensm.*, 1934, **67**, 598–601.)—The method of determining nicotine in fermented tobacco described by Bodnár, Straub and v. Nagy (*Biochem. Z.*, 1928, **195**, 103; 1929, **206**, 410; 1930, **227**, 452) has been found satisfactory by a number of analysts, but others (*e.g.* Dafert and Bollbecher, ANALYST, 1932, **57**, 389) consider that it gives inaccurate results. This method is carried out as follows:—One grm. (0·5 grm. for a high nicotine-content) of the powdered tobacco is mixed in a 50-ml. stoppered cylinder with 1 ml. (0·5 ml.) of 20 per cent. sodium hydroxide solution by means of a small glass rod, which is afterwards dropped into the cylinder. After addition of 20 ml. of a 1 : 1 ether and petroleum spirit mixture, the cylinder is vigorously shaken and left until the tobacco has settled. Ten ml. of the perfectly clear liquid are transferred to a 100-ml. Erlenmeyer flask, which is then heated on a steam-bath until only 1 to 1·5 ml. of a dark greenish-brown, viscous liquid remains (1 to 2 minutes). The flask is at once removed from the bath, 10 ml. of water and 1 or 2 drops of saturated alcoholic methyl red solution are added to the residue, and the liquid is titrated with 0·01 N hydrochloric acid until the greenish-yellow colour changes, fairly sharply, to red: 1 ml. of 0·01 N acid $\equiv$ 1·620 mgrm. of nicotine.

Determinations of the nicotine-contents of a number of fermented and unfermented tobaccos have been made by this method, and also by that of Pfyl and Schmitt (ANALYST, 1927, **52**, 728). The two methods gave results in good agreement, and the maximum difference between four separate results for a single sample of tobacco was the same for the two methods. The micro-method requires practice, and the first results of even a skilled analyst may be subject to various errors, the sources of which are indicated. T. H. P.

Microchemical and Microscopical Identification of Santonin. M. Wagenaar. (*Pharm. Weekblad*, 1934, **71**, 260–264.)—Santonin is usually purified by sublimation (*cf.* Van Zijp, *id.*, 1927, **64**, 278; 1931, **68**, 526), and may then contain artemisin (oxy-santonin), many of the properties of which are similar to those of santonin. The sublimed santonin is soluble in lime-water and forms the calcium salt of santoninic acid; the original crystals, however, are unsuitable for identification under the microscope, and it is advisable to dissolve them in a drop of a mixture of acetone and water, from which santonin crystallises on warming. A preferable method is to use a drop of pyridine (in which santonin is very soluble), a drop of water being then added, when characteristic, thin, sharply-defined rectangular crystals separate, which may be identified under the microscope, particularly if polarised light is used; this procedure serves to detect 1 mgrm. of santonin. Solutions of sublimed santonin in warm strong sulphuric acid, when cooled and diluted with water, deposit hour-glass shaped plates and similar effects result on diluting solutions in warm glycerin. Van Zijp's reaction (*loc. cit.*) is best carried out on a solution of santonin in sulphuric acid, to a drop of which is added, in succession, a drop of water and a drop of a solution of iodine in potassium iodide solution. The resulting precipitate is re-dissolved in acetone, and, on evaporation, well-formed dichroic square crystals result, which are usually yellowish-green to colourless, but are sometimes dark-brown to red, in which case they are produced as rectangles; the latter have been attributed to the periodide of artemisin. Lindo's test (in which a purple colour is produced with solutions in sulphuric acid by the action of ferric chloride) is essentially a test for the lactone group, and may also be carried out with a solution of ferric ammonium alum. The pale red colour produced with an alcoholic solution of potassium hydroxide is not well-suited to microscopical work, but it may be improved and rendered sensitive to 2 mgrms. of santonin if this alkali is replaced by freshly-ignited lime, and glycerin is used as solvent. J. G.

Collected References. Arsenic, Antimony, Tin, and Bismuth. K. Heller. (*Mikrochem.*, 1934, **14**, 369–406.)—References since 1926 are collected for the four elements. In the qualitative section a brief critical summary of the methods is given, together with details of the sensitivities. The references in this section comprise:—General separation 21, arsenic 52, antimony 19, tin 24, bismuth 25. In the quantitative section the methods include spectrographic, gravimetric, volumetric, colorimetric, and electrical methods, as well as application to different materials, such as foodstuffs, gases, and animal tissues. The references in this section comprise:—General 5, arsenic 52, antimony 14, tin 16, bismuth 33. In all, 260 references are given. J. W. M.

New "Spot" Test for Beryllium. A. S. Komarowsky and N. S. Poluektoff. (*Mikrochem.*, 1934, **14**, 315–317.)—A new reagent made by coupling *p*-nitroaniline and orcinol reacts with beryllium; magnesium does not interfere with the test, except when present in relatively large amounts. *Preparation of Reagent.*—A hydrochloric acid solution of 1·38 grm. of *p*-nitroaniline is cooled to 0° C. and diazotised with a cooled concentrated aqueous solution of 0·85 grm. of potassium nitrite, and the resulting solution of *p*-nitrobenzyldiazonium chloride is mixed at 0° C. with a sodium hydroxide solution containing 1·42 grm. of orcinol. On acidifying the mixture the dyestuff is precipitated; it is separated, washed with dilute acid, and water, and dried. A 0·025 per cent. solution in N sodium hydroxide is used. *Test.*—A drop of the reagent is placed on a filter-paper, and followed by a drop of the test solution in a capillary, the point of which is allowed to touch the middle of the fleck. A further drop of reagent is added, and in the presence of beryllium a brilliant orange-red colour appears. The smallest amount recognisable is 0·2γ of beryllium in 0·04 ml. of the test solution; this corresponds with a *concentration limit* of 1 : 200,000. Under the same conditions magnesium gives a yellow-brown precipitate, but this masks the beryllium colour only when the magnesium is present in considerable excess; a preliminary separation must then be made. Calcium, strontium, barium and aluminium do not interfere, neither do the rare-earth metals lanthanum, praseodymium, neodymium, cerium, zirconium and polonium. Zinc gives the same colour, but it is discharged by moistening the fleck with a drop of a 25 per cent. solution of potassium cyanide, so that 0·6γ of beryllium may thus be detected in the presence of 715 times the amount of zinc. Nickel, cobalt, copper, cadmium, and silver, which give coloured hydroxides, interfere, but the interference is prevented by complex cyanide formation. J. W. M.

Physical Methods, Apparatus, etc.

Capillary Index of Certain Vegetable Oils. H. Marcelet. (*Compt. rend.*, 1934, **198**, 2073–2074.)—The volumes of the drops of water and of a sodium hydroxide solution of known strength delivered from a burette into a benzene solution of the fatty acid under examination are measured, and the ratio of the difference of these two numbers to the volume of a drop of pure water is the capillary index or emulsifying power for the fatty acid. (Dubrisay and Picard, *Compt. rend.*, 1923, **177**, 589; 1924, **178**, 205; *Dubrisay, Compt. rend.*, 1925, **181**, 1060, 1142; 1932, **194**, 1076.) This procedure has been applied to various vegetable oils by measuring the volume of 6 drops of water, and subsequently of 6 drops of 0·0016 *N* sodium hydroxide solution in a solution of 1 part of the oil in 100 parts of benzene, the drops being allowed to fall at the rate of 3 per minute. The capillary indices found for certain oils were as follows:—Virgin olive oil, 61 to 65; bright olive, 63 to 69; refined olive, 27 to 33; olive pulp oil, 41 to 48; maize oil, 15 to 19; soya bean oil, 13; sesame oil, 58; and arachis oil, 24. The figures for crude and refined olive oil were confirmed by examining a large number of specimens of various origins representing 421 tons of oil, and the average figures were 66·9 for crude, and 31·4 for refined oil. D. G. H.

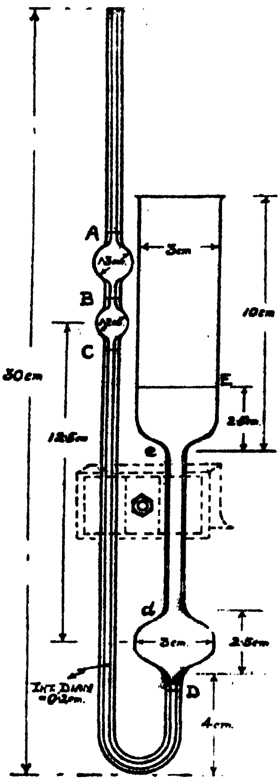
Electro-Magnetic Method of Measuring Specific Gravity. L. R. Bishop. (*J. Inst. Brewing*, **1934**, **40**, 92–94.)—The principle of the apparatus is similar to that employed by Lamb and Lee (*J. Amer. Chem. Soc.*, 1913, **35**, 1666), and its purpose is to provide a check on (and possibly to replace) the specific-gravity bottle method. The liquid under investigation is contained in one of a pair of double-walled vertical tubes, which are used alternately and are filled and emptied at the bottom by means of a suction pump, the liquid being recovered at the end of the measurement in a bottle inserted between the pump and the tube. The tubes, which contain thermometers, are in the form of an inverted cone at the bottom, a solenoid being wound on this portion, so that a current from an accumulator flowing through the wire exerts an electro-magnetic attraction on a hollow soft-iron float in the liquid and causes it to sink. If the current is then gradually reduced until the float just begins to rise again, its strength (*A*) at this point is a measure of the sp.gr. of the liquid. Three small projections on the base of the float prevent it from sticking to the side of the tube, and allow the liquid to drain away, and self-centring of the float with respect to the magnetic field is ensured by the shape of the base of the tube; this shape also produces a rapid acceleration of the rate of rise of the float, since, when the current is just too weak to hold the float down, the latter rises into a weaker magnetic field. The electrical circuit is described and shown in diagram. The apparatus was tested with 96 worts, covering a wide range of specific gravities and temperatures, and the equations found for one tube were:

$$S = 1018{\cdot}375 + 0{\cdot}0339A - 0{\cdot}2038T \pm 0{\cdot}124, \text{ and}$$
$$S_1 = 1021{\cdot}406 + 0{\cdot}0348A \pm 0{\cdot}119;$$

where S is the sp.gr. of the wort (60° F./60° F.), that of water at 60° F. being taken as 1000·000; and S_1 is the apparent sp.gr. at the temperature T (in °C.). Corrections for temperature are given in a table (which applies only to worts), and are calculated from the change in sp.gr. of water with temperature and the results of Day and Amos (*id.*, 1914, **20**, 196). When allowance was made for these, standard errors were obtained for the respective tubes corresponding with 0·4 and 0·5 lb. of extract (10 per cent. worts). The relation between A and S may also be shown graphically. J. G.

Measurement of the Strength of Gelatin Gels. L. H. Lampitt and M. E. G. Norris. (*J. Soc. Chem. Ind.*, 1934, **53**, 179–182T.)—The apparatus devised for measuring gel strength was constructed from a "decimal balance" designed to weigh a load of 10 kilos. The large stirrup and balance pan were replaced by a smaller stirrup and weight pan, and the centre of the pan support was drilled to carry the standard plunger, which consisted of a rod terminating in a hemisphere, 4·5 mm. in radius. A small pan for weights was suspended from the knife-edge originally provided for the weight-pan. The pointer and scale of the balance were retained, since these provided a means of following the plunger movement, which was thereby magnified 10·7 times. A platform on which to place the gels, adjustable in height by means of a screw-thread cut in the base, was mounted beneath the plunger. An aluminium container with a gate control, from which fine, dry, silver sand could be run into a cup on the scale-pan above the plunger, was attached by means of a bar to the central column of the balance. The rate of sand-flow was controlled by the size of the aperture in the gate, which was such that 2·85 grms. of sand per second could pass when the container was full. The rate of flow remained reasonably constant up to 60 seconds, but after this it was reduced, owing to the alteration in the level of the sand remaining in the container. For making a measurement, the balance is adjusted to a 0·1 grm. weight in the pan, until the pointer rests at zero, and the gel is placed on the platform so that the plunger will engage the centre of the surface. The load is applied by opening the sand-control gate, which is shut off when the pointer reaches the 5th scale-division, corresponding with a depression of 4·5 mm. The plunger is lifted, the gel is removed, and the weight required to produce the depression is measured by placing weights on the pan until the pointer balances at zero. The result is multiplied by 10. From the apparent gel-strength the initial load of 1 grm. is subtracted and also the weight required to displace the beam from zero to division 5, the latter constant figure being determined experimentally. The gels are prepared by pipetting 100 ml. of water and putting 17 grms. of gelatin (ground, or in small pieces) in 125-ml. wide-necked bottles with ground glass stoppers, with internal dimensions of 5 cm. in diameter, and 7 cm. from base to shoulder. The bottles are rotated until the gelatin is wet and are then left for 15 to 30 minutes. They are then placed, shoulder deep, in a cold water-bath, and the temperature of the water raised electrically to 67° to 68° C. A control bottle with a thermometer in a similar gel is used with each batch of gels, and at 65° C. the heat is shut off, the bottles are left for 10 minutes, and then removed, and their contents are stirred so as not to produce froth. The bottles are left to cool until the temperature of the control is 30° C., when the stoppers are removed and wiped dry from condensation water, the contents of the bottles are again stirred, the stopper replaced, the bottles are put in a specially constructed water-thermostat maintained at 21° C. ± 0·05° C., for 16 hours, and the strength of the gels is then measured. Results can be satisfactorily reproduced by this method. A comparison of flat and hemispherical plungers was in favour of the latter, since by its use a large depression may be produced without permanent strain, and the degree of accuracy measured may thus be increased. If the ageing period be extended beyond 16 hours, a correction may be made. Between 17° and 23° C. the relation between gel-strength and temperature was found to be practically linear. It is very important to keep the temperature of the gel constant during the ageing period. D. G. H.

An Ostwald Viscometer for Tar. A. R. Lee. (*J. Soc. Chem. Ind.*, 1934, **53**, 69–70T.)—The disadvantage of the Hutchinson and Redwood types of viscometer is the fact that they do not give absolute results; the falling-sphere method is unsuitable for tar on account of the difficulty in locating the sphere in an opaque medium, and the large amount of sample required; and the rotating-cylinder apparatus does not ensure the accurate and uniform temperature control necessary for road tars (for which a change of 0·1° and 5° C. may produce changes of viscosity of 5 and 300 per cent., respectively). The apparatus described gives reproducible results with only 20 ml. of an opaque liquid over a wide range of temperatures, with a timing error of 1 : 1000 even with very viscous tars. It may be completely immersed in a thermostat; readings may be repeated on the same sample for any desired temperature-range without dismantling or cleaning; there is no drainage error; the density of the tar may be neglected if the instrument is suitably calibrated; and the relation between the pressure and the rate of flow may be measured by the use of a supplementary pressure (*vide infra*). The tube *de* in the figure varies from 2 to 6 mm. in length, and serves for viscosities of from a few poises up to 10^6 poises, but the ratio of length to radius must always be the same, so that the rate of shear is constant for the same liquid in the different instruments. A three-way tap above A connects either with atmospheric pressure or with suction, and suction is used to fill the tube accurately with mercury between the marks A and D; the apparatus is then connected with atmospheric pressure, and immersed in hot water, and the tar is poured into the right-hand limb until it reaches D, any air being expelled by the rise and fall of the mercury produced by manipulating the three-way cock. A rubber bung with a glass tube is then placed in the wide limb, and the whole apparatus is allowed to assume the temperature of a thermostat (controlled to within 0·002° C.), the mercury being then sucked up to A, and allowed to fall again under atmospheric pressure, the time (t seconds) for it to pass from B to C being noted. No correction for expansion of the mercury is required at higher temperatures, because the bulb AB allows the mercury to be well within the bulb D*d* before timing begins. The apparatus is calibrated by means of a transparent liquid (*e.g.* syrup), which may be used in the falling-sphere apparatus, or by extrapolation from the values obtained with a smaller viscometer of known constant, the two instruments being filled at the same time and from the same supply, and allowance being made for differences in density (the density of tar varies from 1·14 to 1·26, and may be taken for this purpose as 1·20 for any tar). The viscosity of any tar is given by $\eta = (At - B/t)$, the constants A and B being determined from tests with liquids of widely different viscosities, or with the same liquid at two different temperatures; the error for the abbreviated expression $\eta = Kt$ is less than 1 per cent. Although the design of the apparatus ensures that the driving-pressure is proportional to the difference between the densities of the mercury and the liquid being examined, this pressure may be measured directly by measuring the respective *vacua* required to maintain the level of the mercury at B and at C, and if this method is used for the liquids employed for the calibration and for the test, there is no need to know their densities. The effect of driving-pressure on the rate of flow may be studied by using an auxiliary vessel to produce either a vacuum or an additional pressure. Thus, when an external pressure varying from $-6{\cdot}4$ to $+17{\cdot}1$ cm. of mercury was applied to a syrup known to obey Poiseuille's law, the product of the mean driving-pressure and t varied only between 972 and 998. The time of flow may be controlled by altering the size of the bulb BC; viscosities of 50 and 10^5 poises may correspond with about 15 seconds and 10 to 15 minutes, respectively. The instrument is emptied by bringing the cool tar to the bend below D and inverting the apparatus; it is cleaned by immersion in a hot solution of soap. J. G.



'Capillary'' Int. diam., cm.	tube *de* Length. cm.
0·2	2·5
0·3	3·75
0·4	5
0·5	6·25
0·6	7·5

Reviews

TAUTOMERISM. J. W. BAKER, D.Sc., Ph.D., A.R.C.S., F.I.C. Pp. viii + 332. London: George Routledge & Sons, Ltd. 1934. Price 25s. net.

Of the various subjects usually dealt with as branches of "organic" chemistry, tautomerism is undoubtedly one of the most interesting, and the appearance of a monograph on the subject is very welcome. The wrapper of the book informs us that the work is "a detailed and broad survey of the whole of this field in the light of modern theoretical conceptions," a statement which is virtually repeated in the preface, though qualified by the statement that "although there is a fair measure of agreement amongst chemists with regard to the fundamentals of electronic theory, there is naturally some divergence of opinion in relation to detail. Hence, in attempting to deal with theories which are in such a fluid state of development, it has been considered desirable to adopt a single-minded viewpoint in order to maintain a continuity of argument throughout this monograph."

The above quotation should be kept in mind, for otherwise the reader with a limited knowledge of the subject might receive the impression that practically all the important work had been carried out in the last few years, and so give less credit to earlier workers than they deserve.

Besides the preface, the book contains fourteen chapters and an appendix consisting of the paper read before the Chemical Society on the occasion of the general discussion on May 12th, 1933. The book finishes with subject- and author-indexes which appear to be accurate; the reviewer has found no mistakes in them, except the omission of one acute accent and one *umlaut* sign.

Chapter I is an historical introduction to the subject, and the author sees early glimmerings of the tautomeric idea in Kekulé's dynamic conception of the benzene nucleus and the equilibrium of the two di-*iso*butylenes described by Butlerov in 1877. Erlenmeyer's unsuccessful attempt to isolate vinyl alcohol and the existence of two isomeric methyl-isatins by Baeyer lead to the tautomeric theory of Laar (1885). Mention is made of the oscillation theory of Baly and Desch (isorropesis, 1904), and of the experiments of Lowry and Desch (1909) on the relationship between absorption spectra and isomeric change, which rendered the theory of isorropesis untenable. Meanwhile, Laar's original conception needed modification on account of the work of L. Claisen, W. Wislicenus and L. Knorr. Claisen obtained (1896) two forms of acetyldibenzoylmethane of different melting-points, but both of the same molecular weight—one soluble in sodium carbonate solution and giving a coloured iron salt, the other non-acidic and indifferent to ferric chloride. Enol and keto forms were found to be distinct individuals, and later work has shown that both forms of a tautomeric compound may be isolated in many cases, provided suitable conditions are chosen.

The correlation of tautomerism with reversible additive reactions is treated in Chapter II following the lines laid down by Miss Usherwood (Mrs. Ingold) in 1923, whilst Chapter III deals with the modern theory of tautomeric change. Since the subject is regarded from an electronic standpoint, the names of J. J. Thomson, G. N. Lewis, Langmuir, Robinson, Lowry, and Ingold are found in connection with the electronic characteristics of groups. We are thus led to the consideration of atomic linkage, whether by electrovalency or co-valency, and the concept of the inductive effect naturally follows. The standpoint taken by the author is well illustrated by a quotation (p. 33): "Examples of tautomeric changes known to these early workers were almost exclusively those which involved the migration of a hydrogen atom, and the modern ionic mechanism simply involves an extension of the views outlined above to all types of tautomeric systems, no matter whether the mobile group is a positive hydrogen ion or some other cation (*e.g.* a metal), or whether it is an anion. On this view tautomeric change involves the separation of either a cation or an anion, leaving an electromeric ion (anion or cation respectively), so that the eliminated ion has two possible points of recombination." It is such electromeric ions ("common ions") which chiefly engage the attention of the author, and the location of the charge on such ions is examined at length in the succeeding chapters. These deal with mobility and equilibrium of cationotropic systems (one could wish for a fuller description of experimental methods, both here and throughout the book); dyad, triad and pentad systems, ring-chain tautomerism, valency tautomerism, anionotropy, trans-annular tautomerism and pinacolic electron-displacement.

It will be seen that the work deals with several subjects outside the narrower conception of tautomerism, *e.g.* the "pinacolic electron-displacement" of Ingold and Shoppee, or the theory of Clar as to the cause of colour in the case of *lin*-benzanthracene and *lin*-dibenzanthracene. The book, which is essentially an exposition of the views held by one school as to the cause (and course) of electron displacement in the molecules of carbon compounds, could have been rendered even more complete had the subject of substitution in the aromatic series been considered at length. The reviewer fully admits that this would be outside the purview of a work on tautomerism.

Reference should be made to the Appendix by Professor Ingold, where the "Significance of Tautomerism and of the Reactions of Aromatic Compounds in the Electronic Theory of Organic Reactions" is dealt with. The development of the idea of mesomeric effect and applications to the optical activity of the nitro-anion (Kuhn) and retention of optical activity during the bromination of a ketone (Leuchs and Watke) are especially interesting to some chemists.

Whether the reader agrees with the author in all points or not, he will readily admit the thoroughness with which Dr. Baker puts forward the views of the school he represents. No objection can be taken to this; one is disarmed by the statement in the preface. At the same time one could wish that a fresh edition would handle the experimental side in rather greater detail and assign rather more space relatively to compounds which contain other elements besides carbon, hydrogen and oxygen in the molecule. J. T. HEWITT

QUALITATIVE CHEMISCHE ANALYSE NACH DEM SCHWEFELNATRIUMGANG. By the late GEORG VORTMANN and ROBERT LIEBER. Pp. viii+184. Vienna: Emil Haim & Co. Price 7.50 RM., bound 9.00 RM.

Since 1898 the sodium-sulphide method of qualitative analysis has been in use in the Technical College (Technische Hochschule) in Vienna, in place of the usual hydrogen-sulphide procedure. The original procedure, developed by Dr. Vortmann, has been considerably modified, and the group-divisions described in the present book are:

- I. Sulphides, carbonates and hydroxides insoluble in sodium sulphide solution:
  - A. Sulphides insoluble in dilute hydrochloric acid (1 : 20).
  - B. Sulphides, carbonates and hydroxides soluble in dilute hydrochloric acid (1 : 20).
- II. Sulphides soluble in sodium sulphide.

Tests for alkali metals are made on a separate sample. The method is stated to be cleaner, cheaper, and more rapid; also the analysis is carried out without the necessity for the student to leave his bench, a number of organic compounds may be present without interfering, and tungsten, molybdenum and vanadium can be more easily detected, than in the hydrogen-sulphide procedure.

In this book the procedure described includes tests for a number of less common elements, such as cerium, thorium, zirconium, titanium, beryllium, gold, platinum, tungsten, molybdenum and vanadium.

The tests for cations occupy 100 pages and those for anions 20 pages. They include a number of the modern "spot" tests and tests involving the use of organic reagents. The book is clearly written, and will undoubtedly be of service not only to those who wish to use the sodium-sulphide procedure, but also to all interested in inorganic analysis.

The book might have been improved by a better index, and by a few tabular representations of the separations involved.

JANET W. MATTHEWS

LE ACQUE MINERALI D'ITALIA. QUADERNO PRIMO: LAZIO. Commissione Permanente per le Acque Minerali d'Italia. Pp. viii+239. Rome. 1933.

In abundance and variety of natural waters, Italy probably occupies the foremost place among the countries of Europe. Many of these waters exhibit curative properties, and were famed on this account even in very early days. Later, many of the finest establishments at which the waters were taken either suffered neglect or were destroyed by the barbaric invader. Despite occasional protests, little effort was made to recondition the wells until after the constitution of the Kingdom of Italy, when, following chemical, clinical, and pharmacological investigations, the activity of certain of the spas was revived. This revival has gradually progressed, and is being so stimulated and encouraged under the present régime that Italians no longer need go abroad to take a cure.

The present volume, issued under the authority of a permanent commission presided over by Professor Nicola Parravano, is apparently the first of a number projected, and deals with the waters of Latium. With the help of a number of maps, the geology of the district is described, and, for each of the waters, the chemical, physico-chemical, radio-active, and microbiological properties are given in detail. A separate bibliography is supplied for each of the waters. The make-up of the book is pleasing, and a number of excellent reproductions of pencil sketches of different wells are included. No price is stated.

THE DETECTION OF CRIME: AN INTRODUCTION TO SOME METHODS OF SCIENTIFIC AID IN CRIMINAL INVESTIGATION. By W. M. ELSE and J. M. GARROW. Pp. xxi+195. London: The Office of *The Police Journal*, 69, Great Russell Street. 1934. Price 6s. net.

In this country the scientific investigation of crime is based on a principle different from that adopted on the Continent. With the exception of finger-print investigation, the development of which has been brought to a high state of perfection, the police authorities here rely, in the main, upon scientific assistance from outside, and police laboratories of the type established in many cities abroad are as yet unknown. Both systems have their advantages and their drawbacks, and a combination of both would probably give the best results. If the external system is to be efficient, it is essential that the superior police officers in each area should be well acquainted with the possibilities of scientific examination, and be in a position in every case to call upon the help of the right specialist without delay. Stress is laid upon this point by Dr. Roche Lynch in his foreword to this useful little handbook. The aim of the authors, who hold official positions in the Derby Constabulary and have a wide experience of the difficulties of criminal investigation, has been to give an outline of the principles of the methods used by the outside expert, and thus prevent the loss of valuable evidence through ignorance of what can be done in a given case.

After a preliminary chapter on the training of the faculties of observation and deduction, the authors proceed to the discussion of the various subjects that might require scientific examination and interpretation. There is a chapter on how to search for blood-stains, seminal stains, dusts and soils, and the information on blood-stains is supplemented in a later chapter by a description of the significance of blood-tests, including the determination of blood-groups. Other chapters in this part of the book deal with the identification of hairs and fibres, the examination of handwriting, typescript, and charred papers, the use of dyes and stains in detection methods, the identification of firearms and projectiles, the differentiation of motor tyres (illustrated by a series of plates), preservation of excreta, etc., in toxicological cases, together with points of procedure for the guidance of the policeman.

The second part of the book, headed "Technique," contains seven chapters, dealing with microscopy, photomicrography, and microchemical tests, and is entirely practical. The descriptions are simple and clear, and the authors are obviously giving the results of their own experience. It might, perhaps, be mentioned that they and Superintendent Evans were associated with Professor Brose in working out the fluorescence method of photographing finger-prints described in this journal (ANALYST, 1934, 25). Among the numerous useful sections is one on the structure of the feathers of different species of birds, which is illustrated by plates.

This part of the book is far beyond the scope of the average policeman, and it rather suggests that the Continental system of the police laboratory may not be so far distant after all. Regarded as a whole, the book will be found of value not only by the police, for whom primarily it has been written, but also by the wider public who keep in touch with the scientific investigation of crime; and the authors may be congratulated upon having produced a work that is scientifically sound and full of interest.

At the end of each section are given the names and addresses of specialists who undertake the kind of work described. This is information required by the police, although it would be out of place in a handbook not having such a specific purpose in view.

EDITOR

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GERMAN-ENGLISH CHEMICAL TERMINOLOGY. An Introduction to Chemistry in English and German. By A. KING and H. FROMHERZ. Pp. xvii+324. London: Thomas Murby & Co. 1934. Price 12s. 6d. net.

AIDS TO QUALITATIVE INORGANIC ANALYSIS. By R. G. AUSTIN. Pp. ix+204. London: Baillière, Tindall & Cox. Price 3s. 6d.

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THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS
AND OTHER ANALYTICAL CHEMISTS

The Technique of the Freezing-Point Test for Milk

By G. D. ELSDON, B.Sc., F.I.C., and J. R. STUBBS, M.Sc., F.I.C.

(*Read at the Meeting of the North of England Section, April* 14, 1934)

Our work on the freezing-point test for milk, a test which had, as indeed it still has, such a high reputation abroad, was commenced with the idea of deciding whether it could really be relied upon in this country to detect with certainty the addition of water. The results of many English workers in different laboratories, coupled with our own, have amply demonstrated that this is really a test of "some outstanding significance, yielding information surpassing in reliability that obtained from other tests," and that in this country, as in all other countries where the test has been thoroughly investigated, its indications may safely be accepted.

We have recorded elsewhere (Analyst, 1934, 146) many of the results which we have obtained. In the present paper we have collected together an account of our experience with the Hortvet and the later Monier-Williams cryoscopes —an experience extending to some 3000 determinations.

We have previously stated our objection to a simple form of ice-and-salt cryoscope of the Beckmann type; this objection is based upon the difficulties of manipulation and upon the uncertainty attaching to the temperature of the outer vessel and, in certain methods, to the amount of super-cooling; on all grounds, an ether-cooled cryoscope has distinct advantages. The original Monier-Williams apparatus, whilst admittedly giving results of high accuracy, was, as stated by its designer, too elaborate for routine work. The Hortvet cryoscope has been found to be rapid and convenient, and is so highly regarded that it has achieved widespread acceptance, amounting, in some quarters, to official recognition.

Many times, recently, in the Courts, objection has been taken to the Hortvet method on the ground that it does not give the "true" freezing-point, but the words used in this connection, namely, "it gives wrong results," are far more likely to be misleading than the results themselves. True it is that, as the temperature of the cooling-bath is maintained at some 2·5° C. below that of the freezing-point of milk, whilst the temperature of the milk is rising from the lowest point reached to the point of equilibrium, a certain amount of heat will be lost, causing crystallisation of more ice; a slight increase is caused thereby in the concentration of the solution which will result in a corresponding lowering of the observed freezing-point. This, however, is not a serious objection, as, in any case, the difference so introduced is small, possibly of the order of 0·003° C.; but as different milks are all treated in exactly the same way, the difference will be constant and will not therefore introduce any error, if determinations on unknown milks are compared with those obtained on genuine milks under the same conditions.

An attempt has been made by Monier-Williams in his newer form of cryoscope (ANALYST, 1933, **58**, 254) to eliminate the effect due to abstraction of heat during the time the temperature is rising, while maintaining a rapidity of working comparable with that of the Hortvet apparatus. On theoretical grounds this attempt would appear to have been successful in so far that most of the difference due to this cooling effect has been removed, but we find that a determination takes a much longer time and that, as the heat-insulation is by no means perfect, the amount of ether used is very much greater. While we agree that a value nearer to the "true" freezing-point may be obtained, we cannot see that, for administrative purposes, this is any compensating advantage to make up for practical disadvantages in routine work. Indeed, we whole-heartedly agree with Monier-Williams when he says (*loc. cit.*): "The Hortvet cryoscope is a standardised apparatus, and gives results which, while they do not purport to represent accurately the true freezing-point of milk, *i.e.* the temperature at which milk is in exact equilibrium with ice, are yet strictly comparable and reproducible with a fair degree of precision. . . . Suggestions have been made at various times that the figures should be corrected so as to represent more nearly the true freezing-point of milk, but these suggestions have not usually been adopted, owing, no doubt, to uncertainty as to the nature and magnitude of the corrections to be applied. It has been considered preferable to adhere, for administrative purposes, to the apparent freezing-point, as determined by a standard cryoscope, rather than to confuse matters by attempting to apply corrections which may, or may not, be themselves correct. . . . This is a perfectly sound attitude. . . ."

Having given our views on this point, one which we consider to be of very great importance, we describe some of our experiences with both forms of cryoscope.

THERMOMETERS

(*a*) THE FREEZING-POINT THERMOMETERS.—We have now carried out determinations with three American-made and eight English-made thermometers, and we have regretfully to say that the former are much to be preferred. In the case of some of the English-made thermometers the mercury was apparently dirty, and after a few weeks left a stain in the safety bulb, which later became so marked as to render the thermometer unreliable and useless. Further, whilst we found that the fluctuations in the zero of the American-made thermometers were largely proportional to differences in atmospheric pressure,[*] this factor alone did not explain the variations exhibited by the English-made thermometers.

The earlier English thermometers were provided with two safety bulbs, and it was found that mercury sometimes entered the upper bulb without the lower being completely filled, and it was removed only by the expenditure of much time and trouble. The later English thermometers have only one safety bulb. Two bulbs are not only unnecessary, but a very distinct disadvantage.

It has been stated that in a sensitive thermometer of this type the ascending column of mercury progresses in a series of jerks, and not uniformly. We have carefully searched for this effect, but have been unable to observe it in those thermometers which we have accepted as satisfactory. We have noticed it, however, to a slight extent in one or two of the earlier thermometers which we discarded for other reasons.

It seems to be a fact that each particular thermometer exhibits, during use, characteristics peculiar to itself; indeed, it is almost possible, after considerable experience, to recognise a thermometer from its behaviour in such respects as variation of its zero from day to day, the amount of "lag" and, in some instances, by the elasticity of the bulb causing the mercury momentarily to overshoot the mark to a slight extent before taking up its steady position.

(1) *Specification of the Freezing-point Thermometer.*—The following characteristics of the thermometers used by us have been observed. In some cases the thermometers were returned to the makers before certain observations had been made:

TABLE I

PARTICULARS OF THERMOMETERS

No. of thermometer ..	3261214	305994	2912	26906	292	298	305982
Diameter of stem (mm.)	6·5	6·9	7·0	6·7	—	—	—
Length of 1° „ ..	90	88	87	92	—	—	—
Total length „ ..	596	617	605	620	—	—	—
Length of bulb „ ..	65	61	55	73	—	—	—
Diameter of bulb „ ..	—	9·8	9·0	7·0	—	—	—
Mean zero	—	+0·007	+0·117	—	0·000	+0·024	−0·002

No. of thermometer ..	325 U.S.A.	403 U.S.A.	410 U.S.A.	Empire Marketing Board
Diameter of stem (mm.)	6·7	6·8	7·1	9·8
Length of 1° „ ..	87	103	100	91
Total length „ ..	597	617	621	600
Length of bulb „ ..	52	54	52	59
Diameter of bulb „ ..	9·8	10·2	10·3	10·0
Mean zero	+0·034	+0·032	+0·017	+0·044

As a result of our experience we have found the following dimensions satisfactory for the freezing-point thermometer:

A solid-stem instrument having a total length of 580–600 mm.; the total scale ranging from +1° to −2° C., each degree being divided into tenths and hundredths;

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[*] The changes in the zero do not follow immediately rapid changes in the barometric pressure. There is always a certain amount of "lag," probably due to the imperfect elasticity of the thermometer bulb.

each tenth being numbered. The length of 1° on the scale shall be 90–100 mm. The diameter of the thermometer and the bulb shall be 6·5 to 7·0 mm., and the length of the bulb from 55 to 65 mm. The bulb shall be cylindrical. The safety-bulb at the top of the thermometer shall consist of one compartment only, which shall be in the shape of an inverted pear.

(2) *The Standardisation of the Freezing-point Thermometer.*—According to the American *A.O.A.C. Methods of Analysis*, 3rd Edition, p. 219, the freezing-point thermometer is standardised by determining the freezing-point of pure water and two aqueous solutions of cane sugar containing 7 and 10 grms. of pure sucrose, respectively, in 100 ml. of solution at 20° C. We agree that a weight in volume solution is preferable to a weight in weight solution. Although the latter is capable of being prepared to a greater degree of accuracy, the former can be prepared with much greater ease and with a degree of accuracy well beyond anything which can be obtained in the determination of the freezing-point.

There is sometimes a little uncertainty in securing absolutely concordant results for the freezing-points of these solutions of sucrose when determined in the Hortvet apparatus. The exactness of these figures is of great importance, because upon them will depend all the other results which are obtained.

It will be observed that the two results accepted by the A.O.A.C. for these two solutions, *viz.* 0·422° and 0·621°, have been obtained experimentally in the Hortvet apparatus by means of two thermometers graduated at the Bureau of Standards, Washington, U.S.A. We have gone to some trouble to trace the history of these two thermometers, and as a result of correspondence extending over six months, we have learnt that, whilst the two particular thermometers have apparently been lost sight of, possibly owing to the lamented death of Julius Hortvet, the Bureau of Standards state that they would be correct to about 0·002° to 0·005°, although corrections are given to 0·001°; this is about the degree of accuracy ±0·002° to which the N.P.L. is now able to certify.

It would appear, therefore, that no certifying body can calibrate a thermometer sufficiently accurately for the test,* and that it is necessary to make a standard specifically for the purpose. As the standard suggested by the A.O.A.C. has been in general use for a considerable number of years, there is much to be said in favour of accepting this. It is rather unfortunate, however, that it seems to be more difficult to obtain concordant readings for the freezing-point of solutions of sugar than of many other substances. Thus, whilst it is very unusual for duplicate determinations of the freezing-point of milk to differ by more than 0·001°, we have sometimes found greater variations than this, up to 0·005°, in the case of solutions of sucrose. By making a sufficiently large number of determinations, however, it is possible to obtain a figure which can be accepted as correct, but it might be advisable to experiment with sodium chloride or with lactose, in order to see whether uniformity can more readily be obtained.

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* It should be emphasised, however, that even comparatively large errors in the calibration of the freezing-point thermometer, so long as the scale is uniform, will not cause an erroneous conclusion to be drawn about any particular milk, provided that the reading is compared with those of genuine milks determined under precisely similar conditions. Accurate calibration, however, is essential where the readings of different thermometers are to be compared.

It would appear that the A.O.A.C. tacitly assume that the stem-correction for a thermometer is uniform between the temperatures —0·422° and —0·621°. This is, of course, not necessarily the case, and as neither of these temperatures is one which will be found for the freezing-point of normal milk, we suggest that intermediate points on the scale be taken, calculated from these two values. Such figures are given in the following table, from which it will be seen that solutions of sucrose of 8·5 per cent. w/v and 9·0 per cent. w/v are very suitable for checking the reading of the thermometer at about the freezing-point of normal milk.

TABLE II

Sucrose per 100 ml. of solution at 20° Grms.	Δ*
7·0	0·422
7·5	0·455
8·0	0·488
8·5	0·521
9·0	0·555
9·5	0·588
10·0	0·621

* The symbol Δ is used to represent the depression of the freezing-point below that of water.

With regard to the determination of the zero, it will be observed that the A.O.A.C. (*loc. cit.*) specify that this shall be done with recently-boiled distilled water. We have carried out experiments, the results of which show that the use of boiled or unboiled water makes no appreciable difference to the results obtained. As pointed out by Raoult, the use of unboiled water has the advantage that the amount of dissolved gases will be approximately the same throughout the experiment, but, in any case, the difference to be expected owing to saturation of the water with air, as compared with air-free water, is only about 0·002°.

(*b*) THE CONTROL THERMOMETER.—The control thermometer specified by the A.O.A.C. is of the same external size as the freezing-point thermometer, but has a range of from —30° to +30° C. This range is unnecessarily large, and we have for some time been working with a thermometer having a range of from +2° to —5° C., which has been found to be very convenient in practice. As a result of our work on this thermometer, we have found the following dimensions satisfactory for the control thermometer:

A solid-stem instrument of approximately 58 cm. in length, 6·5 to 7·0 mm. in diameter, and having a scale range of +5° to —5° C., divided into fifths of a degree. The safety-bulb shall be of the same character as that of the standard thermometer.

The Porcelain Milk-Scale.—The scale which is usually fastened to the back of the instrument when sold, and which purports to give the percentage of added water according to the observed freezing-points of adulterated milks, is useless and ought to be abandoned.

Observers should use their own basic figures for the calculation of the added water in those instances where they have not a specimen of the genuine milk from the actual herd in question. In any case, the figure of 0·55°, which appears on the scale as the average freezing-point depression for genuine milk, is somewhat on the high side for this country, and on all grounds the scale should be rejected.

The Dewar Flask.—We have had considerable difficulty in obtaining Dewar flasks of the correct size, but this difficulty appears to have been overcome, for the present at any rate. We suggest a tolerance of 50 ml. in the total capacity of the flask (1000 ml.), and a tolerance of 0·5 cm. in the internal depth (28 cm.). The flask should have cylindrical walls from the base upwards, and should have no constriction at the neck.

The Stirrer.—Quite early in our investigations we realised the labour involved in the working of the stirrer, and our colleague, Mr. R. J. Taylor, devised a mechanical apparatus for driving the Hortvet stirrer from an electric motor. This has now been in use for some years, and has given every satisfaction.* We detach the mechanical stirrer at the onset of freezing and complete the determination by hand.

We have found that the results obtained in the Hortvet apparatus do not vary very much with different amounts of super-cooling. This is shown in the following table:

TABLE III

EFFECT OF SUPER-COOLING IN HORTVET APPARATUS

Number of sample		Temperature of commencement of crystallisation	Observed Δ
87	Lytham St. Annes ..	—0·82°C.	0·570*
		—1·74	0·560
		—1·92	0·562
86	„ „ ..	—0·82	0·570*
		—1·35	0·565
84	„ „ ..	—1·02	0·576*
		—1·39	0·560
		—2·15	0·560
88	„ „ ..	—1·03	0·585*
		—1·44	0·565
		—1·98	0·566

* Mercury rose very slowly and began to fall quickly.

It would appear that a reading of at least —1·35° on the freezing-point thermometer should be reached before crystallisation takes place (*i.e.* a super-cooling of approximately 0·8°); otherwise the mercury rises very slowly, is not steady for any appreciable time before a rapid fall occurs, and it seems that under such circumstances the freezing-point is not attained.

Other workers have, we understand, noticed that the amount of super-cooling appears to have little effect on the observed freezing-point in the Hortvet apparatus. Monier-Williams (*loc. cit.*) thinks that it may be due to the type of the stirring in the Hortvet apparatus. Differences in the mode of stirring may cause small differences in the results obtained, owing to several factors which may not all operate in the same direction.

The Blower.—As in the case of the hand stirrer we have replaced the hand blower by a mechanical blower driven by an electric motor. We have now two switches placed on the lower portion of the right-hand side of the apparatus, one controlling the stirrer and the other the blower, which results in the minimum of labour being involved in a determination. The odour of ether is objected to by some, particularly where the apparatus is used in the dairy; we have successfully overcome this difficulty by sealing up the apparatus and leading the ether-charged air straight into the atmosphere outside the laboratory.

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*Similar appliances can now be obtained commercially.

COMPARISON OF THE HORTVET AND MONIER-WILLIAMS CRYOSCOPES.—We have carried out determinations on the same milk, using the same thermometer, in both the Hortvet and later Monier-Williams cryoscopes. Our results are given in the following table:

TABLE IV

COMPARISON OF THE HORTVET AND MONIER-WILLIAMS CRYOSCOPES

Number of sample		Hortvet	Later Monier-Williams*
G.2415	..	0·517	0·510
41851 Bn.D.	..	0·524	0·518
41852 ,,	..	0·524	0·516
41859 ,,	..	0·546	0·540
41861 ,,	..	0·541	0·535
24977 H.B.D.	..	0·539	0·534
24979 ,,	..	0·541	0·533
47787 By.D.	..	0·537	0·535
47788 ,,	..	0·517	0·512
47792 ,,	..	0·537	0·535

* Uncorrected for super-cooling.

It would appear that the Monier-Williams cryoscope gives results about 0·006° higher, *i.e.* nearer the zero, but we do not think that this is material, so long as comparison is made only between results which have been obtained in the same apparatus.

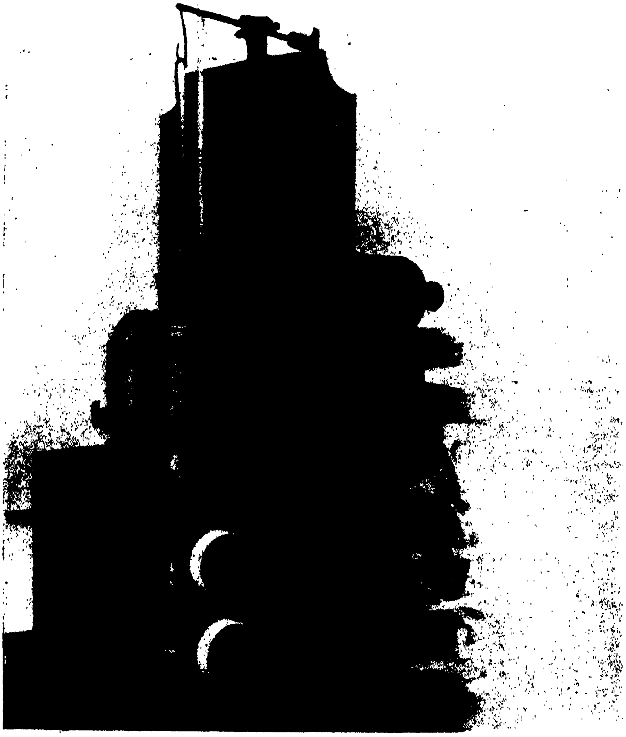
RESULTS BY DIFFERENT OBSERVERS.—Some little time ago a sample of milk was divided into seven portions. The first and last portions were examined in this laboratory, one each of the other five being sent to one of five different analysts who were known to have experience with the Hortvet cryoscope. The freezing-points determined on each of the portions are given in the following table, showing that it is possible to obtain highly concordant results when working with different cryoscopes, different thermometers, and in different laboratories.

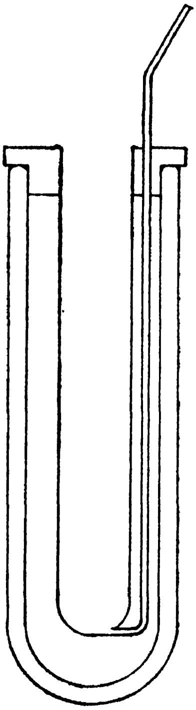
TABLE V

HORTVET RESULTS BY DIFFERENT OBSERVERS

Analyst	Observed Δ
County Lab.	0·549
1	0·551
2	0·552
3	0·549
4	0·551
5	0·549
County Lab.	0·549

Modification of the Hortvet Apparatus.—As previously stated, it is generally acknowledged, and indeed it appears to be a fact, that the results given by the Hortvet technique do not represent "true" freezing-points, that is to say, they are not the exact temperatures at which milks are in equilibrium with ice. From a consideration of the design of the Hortvet cryoscope and of the principles underlying the method of freezing-point determinations, it would seem that it is extremely difficult, and probably impossible, to obtain in this apparatus the data from which "true" freezing-points can be calculated.





We have, however, modified the Hortvet instrument in such a way that it can be used in its original form or on lines similar to the later design of Monier-Williams' apparatus. The accompanying photograph and diagram show how this can readily be done; a metal tube, soldered into the lower end of the tube containing the alcohol, passes upwards through the cork, and is connected with a two-way tap. This tap is connected with a water pump which serves to draw off the alcohol. The method of working is then precisely the same as in the new model of Monier-Williams. We have endeavoured by this means to secure all the advantages of the Monier-Williams apparatus while retaining all those peculiar to the method of Hortvet.

In a subsequent paper we hope to deal with the various corrections applicable to the Hortvet apparatus to determine whether it is possible to develop a method whereby data may be obtained from which true freezing-points can be calculated, as is done in the case of other methods, including that of Monier-Williams.

We do not suggest, indeed we think it unnecessary, that the modified apparatus should be adopted for the purposes for which the original Hortvet apparatus is now used.

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The Absorption of Oxygen by Phosphorus

BY H. R. AMBLER, PH.D., B.SC., F.I.C.

INTRODUCTION.—The absorption of oxygen by solid phosphorus has been widely applied to the determination of oxygen in gaseous mixtures. There has, however, been reason to question the accuracy of this method as commonly used. The sources of error have therefore been examined, and, as a result, it is now shown that it can be made into a precision method.

Over methods involving the use of liquid absorbents it has the advantage that it may be applied to mixtures containing relatively soluble gases such as nitrous oxide.

EXPERIMENTAL

To eliminate error due to physical solution, the phosphorus was confined over mercury (Menzel and Kretzschmar, *Z. angew. Chem.*, 1929, **42**, 148) instead of over water. The phosphorus was used in sticks of about 4 mm. diameter contained in a mercury-filled pipette, about 25 mm. in diameter, fitted at the top with a tap. The sticks were kept damp with water; this avoided gas-locks, and also absorbed the phosphorus pentoxide formed. Gas was measured in an apparatus of the Ambler type (ANALYST, 1929, **54**, 517) of a capacity of 10 ml. and fitted with a phosphorus pipette.

ANALYSES OF AIR.—The process was first examined in the simple case of the determination of oxygen in air. Preliminary determinations showed that, although absorption of oxygen was rapid, results were in nearly all cases low, the apparent oxygen figure ranging from 20·5 to 20·8 per cent., instead of 20·9 to 21·0. In all these experiments the air was left in contact with the phosphorus until fuming had ceased; further contact did not result in further contraction. At temperatures between 18° and 27° C. the time taken for this constant volume to be attained was about 4 minutes.

Examination of the residual gases showed that these low results were due to unabsorbed oxygen (or some very similar gas), and not to the formation of gaseous by-products. Further analyses of air were accordingly made, and quantitative tests for residual oxygen were made by three methods: (i) absorption by pyrogallol solution; (ii) combustion with hydrogen in the presence of heated platinum (ANALYST, 1930, **55**, 677); (iii) the pyrogallol colorimetric test (ANALYST, 1934, **59**, 14).

As is shown in Table I, if the quantities of oxygen so determined are added to those measured by the contraction with phosphorus, accurate results are obtained.

TABLE I

ANALYSES OF AIR BY ABSORPTION WITH PHOSPHORUS AND DETERMINATION OF RESIDUAL OXYGEN

Oxygen found				
Absorbed by phosphorus Per Cent.	Determined in residue Per Cent.		Total* Per Cent.	Method of determination of residual oxygen
20·5	0·2		20·7	Absorption by pyrogallol
20·8	0·1		20·9	
20·8	0·2		21·0	
$20{\cdot}8_5$	$0{\cdot}1_5$		21·0	
20·8	0·2		21·0	
20·9	0·2		21·0	
$20{\cdot}7_5$	0·2		$20{\cdot}9_5$	
20·8	0·2		21·0	
20·8	0·1		20·9	
		Mean	20·94	
20·7	0·05		$20{\cdot}7_5$	Combustion with hydrogen
20·9	0·03		$20{\cdot}9_5$	
20·7	0·1		20·8	
20·7	0·1		20·8	
20·6	0·2		20·8	
$20{\cdot}8_5$	0·15		21·0	
20·9	0·03		$20{\cdot}9_5$	
$20{\cdot}9_5$	0·12		$21{\cdot}0_5$	
		Mean	20·89	
20·7	0·1		20·8	Pyrogallol colorimetric method
20·8	0·1		20·9	
		Mean	$20{\cdot}8_5$	

* Correct figure = 20·93 per cent. (*cf.* Haldane and Makgill, ANALYST, 1933, **58**, 378).

MIXTURES CONTAINING NITROUS OXIDE.—The determination of oxygen in the presence of nitrous oxide has been a matter of considerable difficulty in the past, available methods involving either condensation with liquid air (which may not always be conveniently obtainable) or combustion of the oxygen, together with the nitrous oxide, with hydrogen or carbon monoxide (for details see Lunge and Ambler, *Technical Gas Analysis*, 1934, p. 275 *et seq.*). Menzel and Kretzschmar (*loc. cit.*) made use of the mercury-filled phosphorus pipette for the purpose, but it appears that any effect of unabsorbed oxygen was within the experimental error of the measuring apparatus used. Where nitrous oxide is present, the only method available for the determination of the unabsorbed oxygen is the colorimetric method. Results of some analyses with mixtures containing nitrous oxide, oxygen and nitrogen in known proportions are given in Table II. It is seen that there is no consistent error.

TABLE II

DETERMINATION OF OXYGEN IN PRESENCE OF NITROUS OXIDE

		Oxygen found			
Nitrous oxide Per Cent.	Oxygen taken Per Cent.	By absorption with P Per Cent.	Determined in residue Per Cent.	Total Per Cent.	Error Per Cent.
10	44·2	44·2	0·2	44·4	+0·2
11	34·8	34·5	0·1	34·6	−0·2
12·5	37·2	36·9	0·2	37·1	−0·1
13·5	18·1	18·0	0·1	18·1	0
16·5	45·0	44·6	0·2	44·8	−0·2
20	16·9	16·9	0·05	16·9$_5$	+0·0$_5$
				Mean	−0·04

Table III shows the results of four determinations of oxygen in a gas containing oxygen, nitrous oxide and nitrogen (nitrous oxide approximately 5 per cent.).

TABLE III

REPEAT DETERMINATIONS OF OXYGEN IN A NITROUS OXIDE-OXYGEN-NITROGEN MIXTURE

	Expt. 1	Expt. 2	Expt. 3	Expt. 4
Oxygen absorbed by phosphorus (percentage on total gas)	31·0	30·8	30·8	30·9
Oxygen determined in residue (percentage on total gas)	0·15	0·10	0·16	0·22
Total ..	31·1$_5$	30·9	30·9$_5$	31·1
Mean figure for oxygen	31·0$_2$			
Maximum divergence	0·2$_5$			
Mean divergence from mean ..	0·1$_0$			

ACTIONS CONSEQUENT ON THE ABSORPTION OF OXYGEN BY PHOSPHORUS.—*Effect on Hydrogen and Carbon Monoxide.*—Boussingault in 1864 (*Compt. rend.*, 1864, **58**, 777) published the results of experiments in which it was shown that appreciable quantities of hydrogen and carbon monoxide were oxidised when these gases were present with oxygen in a phosphorus absorption-pipette. Leeds (*Chem. News*, 1883, **48**, 25) and Baumann (*Ber.*, 1883, **16**, 2146; 1884, **17**, 283) also stated that when oxygen was absorbed by phosphorus, oxidation of carbon monoxide present occurred; contrary results were, however, obtained by Remsen and Keiser

(*Amer. Chem. J.*, 1883, **5**, 454; *J.C.S.*, *Abs.*, 1884, **149**, 711; *Ber.*, 1884, **17**, 83). Since then, little or no investigation appears to have been made on the subject.

The present experiments confirm the statements that both hydrogen and carbon monoxide may be attacked.

Hydrogen.—A rather surprising result is that the amount oxidised varies *inversely* with the amount of oxygen initially present. Table IV(A) shows that with mixtures containing about 20 per cent. of oxygen, the contraction on treatment with phosphorus was not in excess of that corresponding with the oxygen absorbed. Table IV(B) shows a further experiment, in which the hydrogen remaining after the treatment with phosphorus was determined by combustion with oxygen in the presence of platinum wire. It is seen that no measurable hydrogen had been oxidised.

Where, however, the oxygen-content was low (3 per cent. or less) appreciable oxidation of hydrogen occurred, as shown in Table V. In these experiments nitrogen freed from oxygen was taken, a measured amount of hydrogen was added, oxygen (in the form of air) was introduced in successive small proportions, and the gas was treated with phosphorus. It is seen that the total contractions with phosphorus were considerably greater than the volumes of oxygen added. Subsequent combustion with excess of oxygen confirmed the fact that hydrogen had been consumed. The amount of hydrogen oxidised is seen to depend also on the hydrogen concentration.

TABLE IV

EFFECT OF PHOSPHORUS OXIDATION ON HYDROGEN (LARGE PROPORTIONS OF OXYGEN INITIALLY PRESENT)

(A)

	Per cent. on total gas	
	Expt. 1	Expt. 2
Oxygen taken	18·85	19·20
Hydrogen taken	9·8	6·7
Contraction with phosphorus	18·8$_2$	18·9$_4$
Residual unabsorbed oxygen (determined by reduction with H_2 and hot wire)	0·02	0·12
Total apparent oxygen found	18·8$_4$	19·0$_6$
Hydrogen attacked (*i.e.* excess of apparent oxygen)	0·0$_1$	—0·1$_4$

(B)

	Per cent. on total gas
Oxygen taken	About 46
Hydrogen taken	13·2
Contraction on reduction with hydrogen and hot wire after treatment with phosphorus	0·2
Hydrogen consumed in above process	0·14
Hydrogen determined in residue	13·0
Total hydrogen found	13·1$_4$
Hydrogen attacked	0·0$_6$

TABLE V

EFFECT OF PHOSPHORUS OXIDATION ON HYDROGEN (SMALL PROPORTIONS OF OXYGEN ORIGINALLY PRESENT)

(A) (About 5 per cent. hydrogen present)

Successive amounts of oxygen added Per Cent.	Contraction with phosphorus Per Cent.	Subsequent contraction on treatment with hot wire Per Cent.	Remarks
0·15	$0{\cdot}1_5$	—	Fuming (not treated subsequently with hot wire)
0·24	0·0	0·3	Fuming
0·05	0·2	0·0	,,
0·26	$0{\cdot}6_5$	$0{\cdot}1_5$	,,
0·22	$0{\cdot}4_5$	0·0	,,
0·27	0·0	$0{\cdot}0_4$	,,
0·65	$0{\cdot}6_5$	$0{\cdot}0_5$	,,

	Per cent.
Total oxygen added	1·84
,, contraction with phosphorus	2·1
,, oxygen not absorbed by phosphorus (determined by reduction)	$0{\cdot}1_7$
,, apparent oxygen	2·27
,, hydrogen consumed in phosphorus pipette	$0{\cdot}4_3$

(Total hydrogen consumed by subsequent combustion with oxygen = about 0·3 per cent.)

(B) (About 50 per cent. of hydrogen present)

Successive amounts of oxygen added Per Cent.	Contraction with phosphorus Per Cent.	Subsequent contraction on treatment with hot wire Per Cent.	Apparent oxygen found Per Cent.	Hydrogen oxidised Per Cent.
2·83	$3{\cdot}0_4$	$0{\cdot}1_1$	$3{\cdot}0_8$	$0{\cdot}2_5$
3·12	$3{\cdot}1_7$	$0{\cdot}2_9$	$3{\cdot}2_7$	$0{\cdot}1_5$
1·32	$1{\cdot}6_9$	$0{\cdot}1_8$	$1{\cdot}7_5$	$0{\cdot}4_3$
0·39	$0{\cdot}8_8$	$0{\cdot}3_7$	$1{\cdot}0_0$	$0{\cdot}6_1$

Total hydrogen oxidised in phosphorus pipette .. $1{\cdot}4_4$ per cent.

Thus, for gases containing more than, say, 10 per cent. of oxygen, no error is caused by the oxidation of hydrogen; if, however, the oxygen-content is less than 5 per cent. the effect is usually appreciable.

Carbon Monoxide.—It is found that with mixtures containing oxygen and carbon monoxide over a wide range of proportions, some carbon monoxide is oxidised in the phosphorus pipette. Such oxidation involves no volume-change, and so does not, in itself, introduce error into an oxygen determination. In practice, however, some of the carbon dioxide so produced may be absorbed by the water in the phosphorus pipette; this gives a high figure for the oxygen-content. If, therefore, it is desired to use the phosphorus method for the precise determination of oxygen in mixtures containing carbon monoxide, the minimum amount of water should be present.

Tables VI and VII show the results of experiments with mixtures containing carbon monoxide.*

TABLE VI

EFFECT OF PHOSPHORUS OXIDATION ON CARBON MONOXIDE (LARGE PROPORTIONS OF OXYGEN INITIALLY PRESENT)

	Expt. 1	Expt. 2	Expt. 3	Expt. 4	Expt. 5
Oxygen taken (per cent. on total gas) (*a*)	15·7	15·4	18·7	16·2	11·3
Carbon monoxide taken	32·5	36·0	12·0	22·0	45·5
Contraction with phosphorus	15·5	15·8	18·7	$16{\cdot}2_5$	11·0
Contraction with alkali (*i.e.* CO oxidised, less CO_2 dissolved in phosphorus-pipette) (*b*)	1·1	0·8	0·05	0·0	0·5
Subsequent contraction with hot wire (alkali present)	0·15	0·0	0·4	0·10	0·30
Residual oxygen found (*c*)	0·05	0·0	$0{\cdot}1_3$	0·03	0·1
Total apparent oxygen found	15·55	15·8	$18{\cdot}8_3$	$16{\cdot}2_8$	11·1
Further carbon monoxide oxidised (*d*) [from (*c*) and (*a*)]	—	0·4	0·13	0·08	—
Total carbon monoxide oxidised [from (*d*) and (*b*)]	1·1	1·2	0·18	0·08	0·5

Table VII shows the effect of phosphorus on adding small successive quantities of oxygen to a mixture of carbon monoxide and nitrogen (about 25 per cent. CO) to which small quantities of oxygen (in the form of air) had been added.

TABLE VII

EFFECT OF PHOSPHORUS OXIDATION ON CARBON MONOXIDE (SMALL PROPORTIONS OF OXYGEN INITIALLY PRESENT; CARBON MONOXIDE INITIALLY PRESENT ABOUT 25 PER CENT.)

	Expt. 6	Expt. 7	Expt. 8	Expt. 9	Expt. 10
Oxygen taken (per cent. on total gas) ..	2·06	0·32	0·29	0·14	0·02
Contraction with phosphorus	$2{\cdot}0_7$	$0{\cdot}8_0$	$0{\cdot}1_0$	$0{\cdot}1_0$	$0{\cdot}1_2$
Contraction with alkali	$0{\cdot}1_5$	0·0	$0{\cdot}0_9$	$0{\cdot}1_8$	$0{\cdot}0_7$
Residual oxygen found (by hot wire in presence of alkali)	$0{\cdot}1_0$	$0{\cdot}0_9$	$0{\cdot}1_3$	$0{\cdot}0_6$	$0{\cdot}0_7$
Total apparent oxygen found	$2{\cdot}1_7$	$0{\cdot}8_9$	$0{\cdot}2_3$	$0{\cdot}1_6$	$0{\cdot}2_0$
Further carbon monoxide oxidised ..	$0{\cdot}1_1$	$0{\cdot}5_7$	0·0	$0{\cdot}0_2$	$0{\cdot}1_8$
Total carbon monoxide oxidised ..	$0{\cdot}2_6$	$0{\cdot}5_7$	$0{\cdot}0_9$	$0{\cdot}1_2$	$0{\cdot}2_5$

Table VIII gives the collected results of analyses of mixtures containing oxygen and either hydrogen or carbon monoxide. It is seen that the oxidation, although somewhat less than that reported by Boussingault, is of the same order.

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* In view of the possibility mentioned above, of the absorption of carbon dioxide in the pipette, oxidation was measured not only by the simple process of measurement of the carbon dioxide produced, but also by taking known initial amounts of oxygen and measuring the amounts remaining after the treatment with phosphorus, as in the hydrogen series.

TABLE VIII

OXIDATION OF HYDROGEN AND CARBON MONOXIDE IN PHOSPHORUS PIPETTE; SUMMARISED RESULTS

	Hydrogen or carbon monoxide present Per Cent.	Oxygen present Per Cent.	Hydrogen or carbon monoxide oxidised Per Cent.	
Hydrogen	6	0·2	0·2	
	50	0·4	0·6	
	50	1·3	0·4	
	50	3·0	0·3	
	10	19	<0·1	
	7	19	<0·1	
	13	40	<0·1	
	18	10	1·1	Boussingault
Carbon monoxide	25	0·2	0·3	
	25	2·0	0·1	
	45	11·3	0·5	
	32	15·5	1·1	
	36	15·5	0·8	
	22	16·2	<0·1	
	12	19	0·1	
	6·5	12	0·9	Boussingault
	7·3	19	1·5	

Nitrous Oxide.—Although, as has been shown, the presence of nitrous oxide does not affect the absorption of oxygen, it does not follow that nitrous oxide is not decomposed in the process; if this occurs, it will not affect the determination, since, although the decomposition of nitrous oxide produces oxygen, such oxygen is absorbed forthwith by the phosphorus, the total volume-change being zero.

Some experiments, in which the nitrous oxide remaining after the phosphorus treatment was determined by reduction with hydrogen in the presence of heated platinum wire, gave figures which were considerably lower than the figures for the nitrous oxide-content of the original gas, determined by other methods. Thus two gas mixtures, found initially to contain 5·0 and 5·8 per cent. of nitrous oxide, gave only 4·4 and 4·6 per cent., respectively, when tested after the phosphorus treatment.*

To confirm this, experiments were carried out in which a known quantity of nitrous oxide was added to a measured quantity of air, the contraction with phosphorus noted, and the gas then treated with hydrogen and heated platinum wire, the figure so obtained being corrected for the unabsorbed oxygen (calculated by difference). Table IX shows that the amounts of nitrous oxide so found were lower than those originally present.

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* The nitrous oxide content of the original gas was determined either by density measurement or by determination of the nitrous oxide and oxygen together by reduction with carbon monoxide in the presence of alkali (see *Technical Gas Analysis*, p. 277).

The accuracy of the hydrogen method for the determination of the nitrous oxide after treatment with phosphorus was checked by separate experiments; two mixtures containing 4·4 and 4·3 per cent. of nitrous oxide gave figures of 4·4 and 4·3 per cent., respectively. The nitrous oxide used in all these experiments was from a cylinder obtained from Messrs. Coxeter, London, and was stated to be 99·99 per cent. pure. It was shown by density measurements to be at least 99·8 per cent. pure, and the oxygen-content was found to be less than 0·01 per cent.

TABLE IX

EFFECT OF PHOSPHORUS OXIDATION ON NITROUS OXIDE (1)

	Expt. 1 Per Cent.	Expt. 2 Per Cent.
Oxygen taken	20·2	19·6
Nitrous oxide taken	6·2	6·5
Contraction with phosphorus	19·9	19·4
Residual oxygen (by difference)	0·3	0·2
Contraction with hydrogen and hot wire	6·2	6·8
Ditto, corrected for residual oxygen	5·3	6·2
Deficit of nitrous oxide	0·9	0·3

Table X shows further experiments, in which the oxygen unabsorbed by the phosphorus was determined by dividing the residual gas into two aliquot parts, one of which was tested for oxygen by the colorimetric method, and the other treated with hydrogen.

TABLE X

EFFECT OF PHOSPHORUS OXIDATION ON NITROUS OXIDE (2)

	Expt. 1 Per Cent.	Expt. 2 Per Cent.
Oxygen taken	18·2	54 (approx.)
Nitrous oxide taken	13·6	22·5
Residual oxygen (measured)	0·1	0·15
Contraction with hydrogen and hot wire	13·7	21·5
Ditto, corrected for measured residual oxygen ..	13·4	$21{\cdot}0_5$
Deficit of nitrous oxide	0·2	$1{\cdot}4_5$

An appreciable amount of nitrous oxide had therefore been decomposed during the oxygen absorption. This decomposition does not appear to be the simple thermal decomposition, since the latter does not ordinarily take place below 800° C. (Menzel and Kretzschmar, *loc. cit.*).

It is seen from the above tables that if the nitrous oxide figure determined by hot wire and hydrogen is not corrected for residual oxygen, the apparent nitrous oxide figure may represent the amount originally taken, the error due to residual oxygen balancing the amount of nitrous oxide decomposed. This might possibly explain the apparent inconsistency on this point between the present work and that of Menzel and Kretzschmar.

The question of the inhibiting effect of nitrous oxide on the absorption of oxygen is dealt with later.

CONDITIONS WHICH INHIBIT THE ABSORPTION OF OXYGEN BY PHOSPHORUS.—As is well known, many gases (*e.g.* olefines, phosphine, hydrogen sulphide) inhibit the absorption of oxygen by phosphorus, even when they are present in very small proportions.

It is also well known that, if the oxygen is present in too large proportions, absorption is inhibited. Where the diluent gas is nitrogen, this limiting proportion of oxygen corresponds to a partial pressure of about 0·75 atmosphere of oxygen; thus oxygen-nitrogen mixtures containing more than 75 per cent. of oxygen do not (at atmospheric pressure) react with phosphorus in the manner characteristic of the weaker mixtures. If reaction does take place, the phosphorus ignites spontaneously and burns violently.

In addition to these inhibiting effects, a remarkable effect of *carbon dioxide* has now been observed. It has been found that, whilst carbon dioxide has not of itself an inhibiting effect, its presence greatly lessens the amount of *oxygen* required to inhibit absorption. Thus the presence of 4 per cent. of carbon dioxide was sufficient to prevent absorption of the oxygen in a gas mixture containing 50 per cent. of oxygen; on the other hand, if the oxygen-content was not more than about 25 per cent., as much as 45 per cent. of carbon dioxide might be present without hindering the absorption. For any one concentration of oxygen, however, the inhibiting effect was greater with greater proportions of carbon dioxide. With some mixtures (containing 15 per cent. of oxygen and 85 of carbon dioxide) no fuming occurred at first, but, after an induction period of about 6 minutes, fuming set in and absorption then proceeded at a rapid rate.

A distinction may be drawn between two types of fuming. Sometimes quite copious fumes may be observed which are not, however, attended by any considerable absorption. Such fumes are fleecy in appearance, and are concentrated in the lower part of the absorption pipette. In contrast to this type of fuming is a turbulent fuming, filling the whole of the space in the pipette and attended by rapid, or at least appreciable, absorption. In some experiments with carbon dioxide (about 10 per cent. of oxygen, 90 per cent. of carbon dioxide) "fleecy" fuming commenced immediately on the entry of the gas; little absorption, however, took place until six minutes after this; a thin column of fumes was then seen to rise from a small part of the surface of one of the sticks. "Turbulent" fuming then rapidly worked up and continued for about five further minutes, when absorption was completed.

It was at first thought that the inhibitions might be due to traces of ethylene in the carbon dioxide (cylinder of high purity supplied by the London Carbonic Acid Co., Ltd.). The gas was accordingly treated with fuming sulphuric acid in order to remove any olefines, but similar results were obtained. Carbon dioxide prepared from marble behaved in the same way.

The action of phosphorus on mixtures containing various proportions of carbon dioxide and oxygen is tabulated in Table X. It is to be observed that, in general, with experiments on inhibiting effects, repeat experiments do not always give exactly the same results. Consequently, Table X indicates only the general relation which is found to exist between composition and inhibiting effect. Carbon dioxide with large proportions of oxygen appears not merely to inhibit absorption, but actually to "poison" the phosphorus; thus, after a mixture of approximately equal parts of carbon dioxide and oxygen had been in contact with phosphorus (no absorption occurring), and the gas was then removed and replaced by air, absorption of oxygen from the air was much slower than is the case with phosphorus which has previously been in contact only with air or non-inhibiting mixtures.

Nitrous Oxide.—The effect of nitrous oxide was examined in a similar way and found to be very much smaller than that of carbon dioxide. Thus, as shown in Table X, a mixture containing approximately 41 per cent. of oxygen and 59 of nitrous oxide behaved in an entirely normal way with phosphorus; the oxygen was absorbed rapidly, no inflammation taking place. With a 50 : 50 mixture, absorption was slower, but no inflammation took place. With a mixture containing 55 per cent. of oxygen and 45 per cent. of nitrous oxide, however, there was very little fuming or absorption. When the same phosphorus was treated with a mixture containing 45 per cent. of oxygen, 37 of nitrous oxide and 18 per cent. of nitrogen, slow absorption occurred; after an induction period of 8 minutes the phosphorus inflamed violently. This violence greatly exceeded that with carbon dioxide mixtures, owing to the thermal decomposition of nitrous oxide and production of further large quantities of oxygen. A "poisoning" effect was noted similar to that with carbon dioxide; thus in this last experiment (Table X) the contact with the previous mixture had had an effect on the phosphorus, since the same phosphorus had previously given normal absorption with a gas containing the same proportion of oxygen and considerably more nitrous oxide.

Since the physical constants of carbon dioxide and of nitrous oxide are very nearly equal, the difference in the effects of these gases indicates that the effect is chemical rather than physical.

TABLE XI

EFFECT OF CARBON DIOXIDE AND NITROUS OXIDE ON THE ABSORPTION OF OXYGEN

	Oxygen present Per Cent.	Carbon dioxide or nitrous oxide* Per Cent.	Observed effects
Carbon dioxide	15	43	Normal fuming and absorption
	19·5	8	,, ,, ,, ,,
	25·5	23	,, ,, ,, ,,
	28·5	22	,, ,, ,, ,,
	50	15	Fuming developed slowly; fuming and absorption appreciable in 6 minutes; inflamed in approx. 10 min.
	15	85	"Fleecy" fuming and little absorption at first. Turbulent fuming and rapid absorption set in within 5 minutes. No inflammation.
	40	60	Little or no fuming or absorption at beginning. Inflamed on standing.
	2	50	Normal type but rather slow absorption.
	52	10·5	Fuming developed slowly; inflamed in 4 mins.
	50	50	No fuming, no absorption.
	49	23·5	,, ,, ,, ,,
Nitrous oxide	12	30	Normal fuming and absorption.
	41	59	,, ,, ,, ,,
	49	51	,, ,, ,, ,,
	45	17	,, ,, ,, ,,
	55	45	Little fuming, slow absorption (5 per cent. O_2 absorbed in 27 minutes).
	45	37	After contact with previous mixture. Fuming worked up slowly; inflamed in 8 minutes.
Carbon dioxide and nitrous oxide absent	46	0	Normal fuming and absorption; no inflammation.
	70	0	Normal fuming and absorption at first; inflamed in 3 minutes.

* The remaining gas, if any, was nitrogen.

CONDITIONS AFFECTING AMOUNTS OF RESIDUAL OXYGEN.—The use of phosphorus for the analytical absorption of oxygen has been described in the preceding sections. A few additional experiments may now be described which were undertaken to determine more definitely the conditions and extent of the absorption.

The incompleteness of the absorption of oxygen might be attributed to (*a*) the necessity for a minimum concentration of oxygen, (*b*) a reaction between phosphorus and oxygen, which generates an inhibitant.

Effect of Concentration of Oxygen.—The pipette was filled with fresh sticks of phosphorus. The measuring vessel of the gas analysis apparatus was filled with nitrogen, and a small quantity (approximately 0·1 per cent.) of air added to it, the amount of air so added being measured by noting the length of capillary tubing (1 mm. bore) occupied by it. The gas was then transferred to the phosphorus-pipette.

The gas was left in contact with the phosphorus for about one minute. No fuming was observed; this showed that absorption was not taking place.* The gas was then transferred back to the measuring vessel, a further small quantity of air being added and the experiment repeated several times.

In series (A) (Table XII) fuming was not observed until a total of 0·2 per cent. of oxygen had been added. Although fuming then took place, a subsequent colorimetric test showed residual oxygen to the extent of about 0·05 per cent. In series (B) (Table XII) successive small quantities were added, up to 0·6 per cent. of oxygen. Fuming did not occur. The gas was then transferred to the measuring vessel and replaced in the phosphorus pipette by air. When fuming had ceased the residual gas from the air was ejected, and the original gas was brought again into

TABLE XII

EFFECT ON FRESH PHOSPHORUS OF VERY SMALL CONCENTRATIONS OF OXYGEN

	Successive amounts of oxygen added to gas Per Cent. (volumes)	Visual effect with phosphorus	
Series A	0·02	No fuming	0·05 per cent. O_2 found subsequently.
	0·05	„	
	0·15	„	
	0·02	Fuming	
	0·03	Just detectable fuming	
Series B	0·03	No fuming	On subsequent treatment with phosphorus which had been treated with air, copious fuming and contraction of 0·4 per cent.
	0·10	„	
	0·11	„	
	0·15	„	
	0·06	„	
	0·13	„	
Total	0·58		

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* Experiments showed that the absorption of 0·03 per cent. of oxygen produced perceptible fuming.

contact with the phosphorus. Copious fuming was observed; the measured contraction was of the same order as the total oxygen added.*

Further successive small quantities of air (0·04 to 0·09, total 0·19 per cent.) were then added, and the gas was treated in the same way. Although slight fuming occurred in most of these cases, subsequent treatment with pyrogallol showed 0·2 per cent. of residual oxygen. Somewhat larger amounts of air (0·1 to 1·3 per cent. of oxygen) were then added. Table XIII shows that the bulk of such oxygen was absorbed.

TABLE XIII

EFFECT ON PHOSPHORUS OF SMALL CONCENTRATIONS OF OXYGEN

Successive amounts of oxygen added to gas Per Cent. (volumes)	Contraction with phosphorus Per Cent.	Visual effect	
0·14	$0{\cdot}1_5$	Definite fuming	Oxygen in residue found to be less than 0·05 per cent.
1·20	1·2	,, ,,	
0·70	0·6	,, ,,	
1·25	1·3	,, ,,	

Formation and Removal of an Inhibitant.—Air was brought into the phosphorus-pipette and left there until fuming had ceased. The residual gas was then removed from the phosphorus, and it and the phosphorus were washed separately with water. The gas was then re-introduced into the phosphorus-pipette. Copious fuming took place, and a considerable proportion of the residual oxygen was absorbed (Table XIV).

TABLE XIV

REMOVAL OF INHIBITANT BY WASHING

	Expt. 1	Expt. 2
Contraction on treatment of air with phosphorus (vol. per cent.)	20·8	20·7
Further contraction on treating washed gas with unwashed phosphorus	$0{\cdot}0_5$	—
Further contraction on treating washed gas with washed phosphorus	$0{\cdot}1_5$	0·3

DISCUSSION ON MECHANISM OF ABSORPTION

It has been shown that:

(1) Although absorption may sometimes occur where as little as 0·03 per cent. of oxygen is present, about 0·5 per cent. is required to ensure it.

(2) Phosphorus which has left unabsorbed small quantities of oxygen may be made to absorb some of it by treatment with air.

(3) Where the concentration of oxygen exceeds a certain amount, absorption does not occur.

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* Eighty per cent. of the oxygen added; the figure for the oxygen added depends on a large number of measurements and is subject to considerable error.

(4) The presence of carbon dioxide, and to a less extent nitrous oxide, lowers the amount of oxygen which is necessary to produce this effect and may also "poison" the phosphorus.

Where the concentration of oxygen is high, an action may take place in which the phosphorus inflames. (This action is further differentiated from the slow absorption in that copious fumes are not produced.)

(5) Absorption of oxygen is not nearly complete, residual oxygen nearly always remaining. Some of this can be absorbed by washing the gas and the phosphorus with water and bringing them into contact again.

These phenomena accord with the hypotheses:

(*a*) Absorption of oxygen depends on the production of an intermediate substance, the formation of which requires a small but definite concentration of oxygen.

(*b*) The reactions between phosphorus and oxygen generate an inhibitant which can be removed by washing.

(*c*) When oxygen is present in large proportions, formation of the intermediate substance is prevented.*

(*d*) Carbon dioxide and, to a less extent, nitrous oxide, assist in preventing the formation of the intermediate substance. They may also generate an inhibitant which "poisons" the phosphorus.

(*e*) Phosphorus and oxygen can also combine by a mechanism which is different from that referred to in (*a*) above, and is probably direct combination. This process does not, however, take place unless the temperature of the phosphorus rises locally.

Nature of the Intermediate Product.—It has been generally accepted that oxygen in its usual form does not react with phosphorus at ordinary temperatures, and that the absorption of oxygen by phosphorus involves the formation of an intermediate substance. The present observations confirm the formation of an intermediate substance, but do not supply evidence of its identity.

The hypothesis has been put forward in the past that this substance is ozone. It is known that ozone is produced in the absorption process, and it has also been remarked that those substances, such as olefines, which most strongly inhibit the absorption are those which also remove ozone. The formation of ozone would not, however, adequately explain all the observed phenomena; in the present investigation, for example, ozone has been detected in the gas remaining after treatment of air with phosphorus.†

Ozone would also not explain the oxidation of hydrogen and carbon monoxide. The controversy between Leeds and Baumann on the one hand, and Remsen and Keiser (*loc. cit.*) on the other, was concerned with the evidence for the formation of an active form of oxygen other than ozone; the question remained unsettled, however, on account of disagreement on a point of fact, namely, the oxidation of carbon monoxide. As is detailed earlier in this paper, the present investigation conclusively confirms the results of Leeds and of Baumann on this issue, and affords grounds for the re-opening of the discussion as to the formation of such a hypothetical form of oxygen.

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* The existence of an intermediate substance which is destroyed by high oxygen-content is supported by the observation, recorded earlier in this paper, that hydrogen, in the presence of phosphorus, is oxidised most readily where the concentration of oxygen is *small*.

† Tested by smell and by iodide-starch paper.

SUMMARY.—1. Phosphorus used as an absorbent for oxygen may leave unabsorbed quantities of the order of 0·2 per cent.

2. If these small quantities of residual oxygen are subsequently determined, a precision method of analysis for oxygen-nitrogen mixtures is attained.

3. By means of this method, oxygen in the presence of nitrous oxide can now be determined precisely.

4. When gases containing oxygen and hydrogen are treated with phosphorus, hydrogen up to about 0·5 per cent. may be oxidised. The effect is greatest where the amount of oxygen originally present is small. Carbon monoxide is oxidised to a rather greater extent.

5. When gases containing oxygen and nitrous oxide are treated with phosphorus, appreciable quantities of nitrous oxide may be decomposed. This does not, however, interfere with the determination of oxygen.

6. The presence of carbon dioxide greatly decreases the maximum concentration of oxygen above which absorption is inhibited. Nitrous oxide has a similar, but much smaller, effect.

7. The mechanism of the absorption of oxygen by phosphorus is discussed, and evidence is given for the formation of both a necessary intermediate substance and an inhibitant.

RESEARCH DEPARTMENT
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Notes on the Grinding of Feeding Stuffs in a Power Mill

BY F. J. ELLIOTT, M.SC., PH.D., A.I.C.

THE use of power-mills for the reduction of analytical samples is now almost universal in agricultural laboratories. Such mills, indeed, are essential where large numbers of grass and fodder samples are handled in connection with investigational work. During the past four years I have used a mill of the pulveriser type, which is belt-driven at a speed of 7600 R.P.M. by a 2 H.P. motor. The ground sample passes through a sieve into a sealed drawer, above which a dust balloon is fastened. As a result of its compactness and all-round efficiency this type has attained a large degree of popularity among agricultural chemists.

In the course of recent work carried out by the Agricultural Education Association it was observed that representative samples of grass drawn from a homogeneous bulk, when re-ground and examined at a number of different centres, showed discrepancies in crude protein-content which could not be attributed to sampling error, or to any ordinary variation in laboratory technique. It was suggested that the differences observed might have resulted from the use of mills of widely varying character, some of the laboratories concerned having employed power-mills of the most modern type, whilst in others only obsolete, hand-operated mills were available.

The object of this short investigation was to determine whether the use of a modern power-mill did reduce the crude protein-content of fodder samples to any significant extent and, if possible, to ascertain the cause of this effect.

One thousand grms. of a poor meadow-hay were passed through an ordinary household mincer. The material was then mixed by hand for fifteen minutes and divided into five equal portions, one of which was bottled without further treatment. The remaining portions were ground in the power-mill to pass the 1/8, 1/16, 1/32, and 1/64-inch sieves respectively. Five replicate nitrogen determinations were made on each of the five samples by the usual Kjeldahl method. In each case the total crude protein-content was calculated by multiplying the percentage of nitrogen found by 6·25. At the same time the moisture-content of each sample was determined in duplicate by drying five grms. for a period of 24 hours in an electric oven maintained at 100° C.

The results obtained are tabulated below.

TABLE I

PER CENT. OF TOTAL CRUDE PROTEIN IN DRY MATTER

		Power Mill			
	Mincer	1/8″ sieve	1/16″ sieve	1/32″ sieve	1/64″ sieve
	9·61	9·39	9·40	9·08	9·34
	9·81	9·49	9·31	9·27	9·34
	9·91	9·49	9·22	9·46	9·24
	10·00	9·39	9·22	9·35	9·24
	9·75	9·39	9·31	9·26	9·34
Mean	9·816	9·430	9·292	9·284	9·300

The analysis of variance and the standard error appertaining to the above figures are shown in Table II.

TABLE II

Variance	Degrees of freedom	Sum of squares	Mean square	Standard deviation	½ log.e mean square	*z*	P
Within classes	20	0·2139	0·0107	0·103	0·0338	—	—
Between classes	4	1·0305	0·2576	—	1·6244	1·5906	<0·01
Total	24	1·2444	0·0519	—	—	—	—

A difference of 0·150 between any two means is necessary for significance (P = 0·05) (Fisher, *Statistical Methods for Research Workers*, 1932). It is evident, therefore, that there is a highly significant difference in protein-content between that portion of the sample which has been ground in the mincer and the remaining four portions which have been passed through the power-mill. The apparent difference between the means for the 1/8-inch sieve sample and the means for the three other milled samples cannot be considered a real one.

In order to ascertain whether the same effects were produced with a high protein concentrate, the above procedure was repeated with 1000 grms. of decorticated ground nut-cake. Table III embodies the results obtained on this material.

TABLE III

	Mincer	Power Mill 1/8″ sieve	1/16″ sieve	1/32″ sieve	1/64″ sieve
	57·54	55·51	55·90	55·68	55·35
	57·54	55·70	55·99	55·86	55·16
	57·54	55·51	56·09	56·05	55·16
	57·16	55·33	55·90	55·86	54·98
	57·16	55·70	55·99	55·86	55·35
Mean	57·388	55·550	55·974	55·862	55·200

The difference for significance between any two means, calculated as in the previous example, is 0·220. A large and highly significant difference between the sample ground in the mincer and the remaining four samples is again observed. The means of samples milled to pass the 1/8-inch and 1/64-inch sieves are both slightly, but significantly lower, than the other two milled samples.

The above results show that, both in the case of a coarse fodder of low protein-content and a high protein-concentrate, the use of a power-mill results in a highly significant loss of nitrogenous material. In the case of the hay it does not appear that the varying degrees of fineness of division attained by milling exerted any significant effect on the mean protein-content. Certain significant differences between the means of the milled ground nut-cake have been indicated above. No explanation of the fact that the mean figure relating to the 1/8-inch sample is significantly lower than that appertaining to the 1/16 and 1/32-inch samples can be offered.

The loss, through the balloon, of dust richer in nitrogen than the bulk of the material milled, appeared to offer a likely explanation of the observed decline in protein-content. That a certain amount of very finely divided material is not retained by the balloon is obvious when milling is in progress. In order to estimate the magnitude of this loss, 2500 grms. of the hay previously used were ground in the mincer. After being mixed for 15 minutes, five 400-grm. portions were drawn from the bulk and milled to pass the 1/32-inch sieve. In each case the contents of box and balloon were carefully collected and weighed separately. The percentages of material thus recovered are shown in Table IV, and the total crude protein-content of the fractions in Table V.

TABLE IV

	In box Per Cent.	In balloon Per Cent.	Loss Per Cent.
	90·53	5·75	3·72
	87·50	8·48	4·02
	89·95	6·53	3·52
	87·75	8·80	3·45
	81·90	14·68	3·42
Mean	87·53 ± 1·53	8·85 ± 1·57	3·63 ± 0·11

TABLE V

TOTAL CRUDE PROTEIN IN DRY MATTER

	Sample from box Per Cent.	Sample from balloon Per Cent.
	9·20	11·82
	9·10	11·80
	9·18	11·94
	9·34	11·87
	9·23	11·86
Mean	9·21	11·86

It appears from Table IV that when five hay samples, each of 400 grms., are milled to pass the 1/32-inch sieve the mean loss of material will be between 3·52 and 3·72 per cent. on nineteen occasions out of twenty. On the assumption that the mean weight of dust lost on the present occasion, *viz.* 3·63 per cent., has the same protein-content as the material in the balloon, 41·14 per cent. of the difference between the means in columns 1 and 4, respectively, of Table I will be accounted for. On the other hand, if the former fraction contains a substantially higher protein-content than the latter, then it is probable that the difference is accounted for in full. It is obviously impossible to determine the crude protein-content of the fraction lost, but there will be some justification for assuming that this figure is higher than that appertaining to the fraction in the balloon, if it can be shown that the latter is significantly greater than the protein-content of the material remaining in the box. It will be seen from Table V that the mean protein-content of the material in the box is 9·21 per cent., as against 11·86 per cent. in the balloon. The actual difference necessary for significance is only 0·11 per cent.

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Notes on the Determination of Chromium in the Presence of Iron, Aluminium, and Phosphoric Acid, with Perchloric Acid as Oxidising Agent

BY J. HASLAM, M.SC., A.I.C., AND W. MURRAY

(*Read at the Meeting of the North of England Section, April* 14, 1934)

RECENTLY we became interested in the determination of chromium in various paint-pigments, and certain results which we obtained led us to doubt the accuracy of methods depending on the oxidation of the chromic ion to chromate by means of sodium peroxide, particularly when reasonable amounts of iron were also present.

Järvinen (*Z. anal. Chem.*, 1928, **75**, 1), in a paper dealing with the determination and separation of chromium, iron, aluminium and phosphoric acid in presence of one another, describes in detail the results of his investigation of the various methods of oxidation of chromium to chromate, these methods including the use of sodium hypochlorite, sodium hypobromite, sodium peroxide, potassium permanganate and potassium persulphate, and his results pointed to the conclusion that the most efficient oxidising agent tried was sodium hypobromite.

Iron, aluminium, chromium and phosphoric acid are usually precipitated together in analytical work, and the correct determination of the chromium in such a mixture is a problem with which one is often confronted. Järvinen's method of attack on such a problem is as follows:—

> "The solution (about 100–200 ml.) containing iron, chromium, aluminium and phosphoric acid, is treated with 1 to 2 ml. bromine, and 2 *N* caustic soda solution added until a slight excess (about 10 ml.) is present. After standing for about a quarter of an hour, the precipitate is dissolved in the smallest possible quantity of hydrochloric acid, and the solution again made alkaline. After warming on the water-bath for some time, the mixture is acidified and diluted, and the bromine boiled off. Excess of 2 *N* ammonium phosphate solution is added, and the iron and aluminium precipitated as phosphates by the dropwise addition of concentrated ammonia solution, the whole being then diluted to a definite volume (500 ml.) and filtered. Two hundred-and-fifty ml. of the filtrate are acidified with sulphuric acid, potassium iodide solution is added, and the liberated iodine titrated with N/10 sodium thiosulphate solution. . . ."

We have investigated this method, using chromic solutions prepared by reducing known volumes of *N*/10 potassium dichromate solution with sulphurous acid in the presence of hydrochloric acid, together with known amounts of ferric chloride, aluminium chloride, and phosphoric acid. The results we obtained are given on p. 612 under the heading "Results obtained by Järvinen's Method."

In the first three experiments, where iron was absent, and where the oxidation took place in one phase, all the reactants being in solution, we obtained very satisfactory conversion of the reduced dichromate solution to chromate, but, in the remaining four, where iron was present, the results obtained were always low. These results are not altogether surprising in view of some statements made by Järvinen in his paper. He points out that when a solution of chromic chloride is neutralised with caustic soda solution, the precipitated hydroxide dissolves readily in excess of alkali, but if about the same quantity of ferric chloride is present, and an excess of alkali is added, the chromium hydroxide does not re-dissolve and the filtrate is colourless.

The chromium is held fast by the ferric hydroxide, and this fact may explain why chromium, in the presence of iron, is oxidised with greater difficulty.

Järvinen asserts that a double oxidation is necessary, and a modified double oxidation is actually carried out in his method, outlined above, but our results do not indicate that this ensures quantitative oxidation of the chromium to chromate when reasonable amounts of iron are also present.

Our attention was then directed to a method of oxidation of chromium proposed by Lichtin (*Ind. Eng. Chem., Anal., Ed.*, **1930**, **2**, 126), in which all the reactants are in solution, and difficulties due to the presence of insoluble ferric compounds in suspension in the oxidation process are avoided.

The oxidising agent used is perchloric acid, which Lichtin used in the determination of chromium in chrome alum liquors and crystals, and further work on the use of this reagent has been carried out by Willard (*Ind. Eng. Chem., Anal. Ed.*, **1931**, **3**, 88). We were unaware of Willard's work at the time we began our own, and, consequently, in our investigation have used Lichtin's technique, with modifications.

Lichtin and Willard disagree as to the mechanism of the oxidation, but Willard's explanation appears to be the more probable. He maintains that dilute perchloric acid, which, under ordinary conditions is extremely stable and is not affected by the ordinary reducing agents, on concentration to about 70 to 72 per cent. distils at about 203° C., a certain amount of decomposition taking place, thus: $4HClO_4 = 2Cl_2 + 7O_2 + 2H_2O$. The oxygen liberated under these conditions renders the concentrated acid an extremely powerful oxidising agent.

After carrying out oxidations of chromium to dichromate by means of perchloric acid, and removing iron and aluminium by precipitation as hydroxides, Lichtin determined the dichromate produced; the acidified dichromate solution was treated with potassium iodide solution, and the liberated iodine was titrated with standard sodium thiosulphate solution.

We have found that the dichromate produced in the oxidation is more accurately determined by Knop's method (*J. Amer. Chem. Soc.*, 1924, **46**, 263), which does not involve preliminary removal of iron and aluminium as hydroxides.

A known volume of a standard aqueous solution of chromic anhydride (A.R.), contained in an Erlenmeyer flask, was acidified with sulphuric acid (20 per cent.), and reduced by the passage of sulphur dioxide gas.

After the excess sulphur dioxide had been removed by boiling, 5 ml. of perchloric acid (A.R. 60 per cent. approx.) were added, and the solution was heated on the sand-bath, a small funnel, the stem of which had been removed, being placed in the neck of the conical flask to prevent loss by spurting. When the volume of the solution was considerably reduced by the heating, the oxidation to the orange dichromate took place almost instantaneously, after which the heating was continued for about five minutes.

The flask was removed and allowed to cool, about 100 ml. of water were added, and the solution was boiled until any free chlorine was removed. The cooled solution was diluted to 150 ml., and an excess of *N*/10 ferrous ammonium sulphate solution was added, this excess being determined by titration with *N*/10 potassium dichromate solution, diphenylamine being used as internal indicator (Knop, *loc. cit.*).

The experiment was repeated with the addition of known amounts of ferric sulphate, aluminium sulphate and phosphoric acid, very satisfactory results being obtained, as indicated by those given under the heading "Results obtained by the use of the modification of Lichtin's Method," Experiments 8 to 14 (p. 612).

There are two results, however, which call for comment, and these are given under Experiment 14.

In this case the aqueous solution of the chromic anhydride was reduced in the presence of 2 ml. of concentrated hydrochloric acid, instead of 2 ml. of dilute sulphuric acid solution, so that the final oxidation was carried out in the presence of chloride. The perchloric acid vapour was definitely yellow in colour, and the presence of volatile chromium compounds in the vapour was proved by carrying out a similar oxidation in a round-bottomed flask to which a glass condenser was attached by means of a ground-glass joint, the drawn-out tube of the condenser

RESULTS OBTAINED BY JÄRVINEN'S METHOD

	Added	Found $N/10$ potassium dichromate solution ml.
1	20·0 ml. of $N/10$ potassium dichromate solution	20·02
2	20·0 ml. of $N/10$ potassium dichromate solution 0·04 grm. of aluminium	20·00
3	20·0 ml. of $N/10$ potassium dichromate solution 0·04 grm. of aluminium 0·05 grm. of phosphoric acid	19·97
4	20·0 ml. of $N/10$ of potassium dichromate 0·04 grm. of iron	18·47
5	20·0 ml. of $N/10$ potassium dichromate 0·04 grm. of iron 0·05 grm. of phosphoric acid	18·57
6	20·0 ml. of $N/10$ potassium dichromate 0·04 grm. of iron 0·04 grm. of aluminium	17·5
7	20·0 ml. of $N/10$ potassium dichromate 0·04 grm. of iron 0·04 grm. of aluminium 0·05 grm. of phosphoric acid	17·82

RESULTS OBTAINED BY A MODIFICATION OF LICHTIN'S METHOD

8	(*a*) 19·97 ml. of $N/10$ dichromate (*b*) 19·97 ml. of $N/10$,,	(*a*) 19·96 ml. of $N/10$ dichromate (*b*) 19·94 ,, ,, ,, ,,
9	19·97 ml. of ,, ,, 0·036 grm. of aluminium	19·97 ,, ,, ,, ,,
10	19·97 ml. of $N/10$ dichromate 0·035 grm. of iron	19·91 ,, ,, ,, ,,
11	19·97 ml. of $N/10$ dichromate 0·31 grm. of phosphoric acid	19·94 ,, ,, ,, ,,
12	19·97 ml. of $N/10$ dichromate 0·035 grm. of iron 0·036 grm. of aluminium	19·95 ,, ,, ,, ,,
13	19·97 ml. of $N/10$ dichromate 0·035 grm. of iron 0·036 grm. of aluminium 0·31 grm. of phosphoric acid	19·94 ,, ,, ,, ,,
14	(*a*) 19·97 ml. of $N/10$ dichromate (*b*) 19·97 ,, ,, ,, ,,	(*a*) 19·57 ,, ,, ,, ,, (*b*) 18·93 ,, ,, ,, ,,

dipping into about 10 ml. of water contained in a small beaker. When the oxidation was complete the condenser was washed down with water, and the washings were added to the contents of the receiver.

This aqueous solution was rendered faintly ammoniacal, then just acid with acetic acid and evaporated to a small bulk. The evaporated solution gave the reaction for silver chromate when tested with aqueous silver nitrate solution, and the reaction for lead chromate with aqueous lead acetate solution. A further portion, when treated with hydrogen peroxide, sulphuric acid and ether, gave the characteristic blue oxidation-product of chromium, soluble in the ether.

There is little doubt, therefore, that this behaviour is due to the production of volatile chromyl chloride when perchloric acid oxidations of chromium are carried out in the presence of chlorides, and, in our opinion, chlorides should be excluded from such oxidations.

The behaviour of manganese is interesting. Our experience is that manganese, in reasonable quantity, gives rise to a higher oxide of manganese which interferes in the final titration of the dichromate, and, when considerable quantities of manganese are present, it is probably best to separate the bulk of this element by the preliminary isolation of the hydroxides of iron, aluminium and chromium, etc., with ammonia before proceeding to the perchloric acid oxidation.

There are several very interesting applications of this perchloric acid oxidation process. Such substances as ferrochrome are readily attacked by perchloric acid, and we have determined the chromium in such alloys by direct oxidation with perchloric acid, the dichromate produced being titrated by Knop's method.

Such refractory substances as chrome-iron ore may be disintegrated by fusion with potassium bisulphate in a silica crucible, in accordance with Schoeller's technique; the melt is leached with dilute acid, and metals precipitated by hydrogen sulphide are removed, and, after oxidation of the iron with dilute nitric acid, the mixed hydroxides of iron, aluminium and chromium are precipitated with ammonia. The hydroxides are filtered off, washed with water, and dissolved in dilute perchloric acid solution, and this solution is evaporated until oxidation of the chromium takes place, the dichromate produced being subsequently determined by Knop's method.

We wish to express our thanks to the directors of Imperial Chemical Industries, Limited, for permission to publish this work, which was carried out in the Research Department of their subsidiary company, I.C.I. (Alkali), Limited, Northwich.

The Determination of Volatile Oils in Herbs, Spices and Drugs

By C. EDWARD SAGE, F.I.C., and H. RONALD FLECK

THE value of many herbs and drugs depends on their aromatic constituents, and the volatile oil which they contain may be the only constituent of any value. Once that is lost by any means, the substance may become almost worthless.

In the course of general analytical work, it is often needful to have some definite statement regarding the amount of volatile oil in a particular sample, and the choice of a method of determining this raises difficulties, for often only small quantities are available for examination.

The United States Pharmacopoeia makes approximate determination of such constituents by extracting the substance with ether, and differentiating between the volatile and non-volatile portions of the extract, and by these means evaluates such substances as cloves and cubebs, which contain notable proportions of volatile oils. The method may be of some service, but it very effectually prevents any examination of the volatile portion of the extract.

Several drugs are used in a state of powder for the preparation of well-known products specified in the British Pharmacopoeia; for instance, aromatic powder of chalk contains cinnamon, nutmeg, clove and cardamons; compound liquorice powder contains powdered fennel; confection of senna contains coriander. Many other drugs contain volatile oil as their most important constituent. Some of these are amenable to the volatile-ether-extract process, but some other means are needed whereby they may be examined for either purity or reasonable freshness.

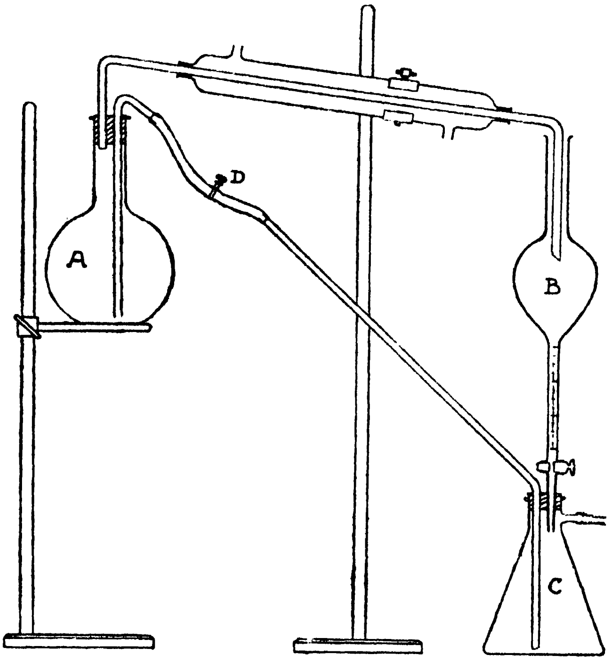
The aromatic domestic herbs also need examination for similar reasons, and dried mint, thyme, marjoram, basil and savory, each contains its own peculiar volatile oil on which it depends for its suitability for flavouring purposes.

Veterinary medicines contain such ingredients as anise, cummin and foenugrec, and the confectionery trades make use of angelica, whilst the distillers use considerable quantities of juniper berries and anise.

In the course of many years' experience of the extraction of essential oils from these substances, it has often been necessary to give an opinion on the value of quite small samples, and, in view of its service, the following description of an arrangement of apparatus for determination of the proportions of volatile oil may serve as a guide towards a standard method for the necessary process of extraction, and some limits to be permitted for volatile constituents.

It cannot be claimed that the examination by the method described will be as accurate as distillation of large bulks of either substance mentioned, but the laboratory test will serve as a pilot for the factory, or enable an analyst to state if a sample is deficient in its all-important constituent.

DESCRIPTION OF APPARATUS.—The boiler A is an ordinary 1-litre flat-bottomed flask, and is connected with a Liebig condenser, having a narrow-bore inner tube bent as shown. The receiver B is a standard separating funnel receiver (V.4), as specified by the Standardisation of Tar-Products Tests Committee, and C is a 250-ml. Buchner flask. The flask C is connected with A by means of a glass tube with rubber connection, and Hofmann screw-clip at D. The liquid in A is boiled, the distillate is collected in B, and after 100 ml. or so has come over, the lower aqueous layer is separated and pumped back into A by opening the clip at D, and applying a small hand-bellows at C. This cycle is repeated several times until no more oil passes over.



The size of the distillation flask may be varied according to the bulk of the material examined, but the accompanying figures were all obtained when using a 1-litre vessel.

For oils which sink in water, the separation is accomplished by placing a measured volume of toluene in the separator, which enables the oily mixture to float, allowance being made for this when making the final measurement.

Solubility of the oil in the distillate cannot be allowed for with any precision, but the repeated distillation of the separated water leaves the bulk of the oil for measurement, and the accuracy of a series of determinations is checked by starting a blank experiment with a known volume of oil.

For purposes of comparison, we have determined the volatile ether extract in some of the samples, and the figures obtained afford useful comparisons and confirmation of the results obtained by distillation.

Among the advantages claimed are the mobility of the apparatus, and the short time it takes to obtain results which are of practical utility. In most instances sufficient volatile oil is obtained with which to take a reading of its refractive index, and some of the oils permit of a determination of an important constituent.

CULINARY HERBS

MINT

Sample	Oil Per Cent. v/w	n_D^{20} of oil
1	0·84	1·4914
2	0·10	1·4937
3	0·92	1·4860
4	0·40	1·4924
5	1·41	1·4857
6	1·20	1·4860
7	1·10	1·4928

The volatile ether extract of sample No. 1 was 0·78 per cent. w/w. *Useful limits.*—0·80 to 1·20 per cent. of oil. n_D^{20}, 1·4855 to 1·4940.

THYME

Sample	Oil Per Cent. v/w	n_D^{20} of oil
1	1·84	1·4940
2	1·44	1·4949
3	1·32	1·4951
4	0·64	1·5028
5	1·64	1·5121
6	1·40	1·4933
7	1·40	1·4925
8	1·80	1·5016
9	1·46	1·4953
10	1·36	1·4968
11	1·32	1·4973
12	1·40	1·4955
13	1·76	1·4906
14	1·30	1·4914

No. 5 was a lemon thyme.
The volatile ether extract of sample No. 1 was 1·9 per cent. w/w.
Useful limits.—1·20 to 1·80 per cent. of oil. n_D^{20}, 1·4905 to 1·5030.

MARJORAM

Sample	Oil Per Cent. v/w	n_D^{20} of oil
1	0·88	1·4930
2	2·08	1·4928
3	2·52	1·4837
4	1·84	1·4870
5	1·84	1·4872
6	0·32	1·4824
7	1·12	1·5021
8	1·12	1·5030
9	0·80	1·5002
10	2·24	1·4882
11	2·04	1·4833

The volatile ether extract of sample No. 1 was 0·92 per cent. w/w. *Useful limits.*—1·80 to 2·50 per cent. of oil. n_D^{20}, 1·4830–1·5030.

Basil

Sample	Oil Per Cent. v/w	n^{20}_{D} of oil
1	0·18	1·4858
2	0·10	1·4802
3	0·13	1·4967

The volatile ether extract of sample No. 1 was 0·20 per cent. w/w.

Parsley

Sample	Oil Per Cent. v/w	n^{20}_{D} of oil
1	0·10	1·5159

The volatile ether extract was 0·09 per cent. w/w.

Sage

Sample	Oil Per Cent. v/w	n^{20}_{D} of oil
1	1·16	1·4651
2	1·33	1·4655
3	1·12	1·4660
4	1·04	1·4623
5	1·18	1·4662
6	1·34	1·4633

No. 1 was a French sage, Nos. 3, 4 and 5, Dalmatian, and No. 6, a bulk sample. The volatile ether extracts of samples Nos. 1 and 2 were 1·13 and 1·40 per cent. w/w.

Savory

Sample	Oil Per Cent. v/w	n^{20}_{D} of oil
1	0·94	1·4943

Drugs and Spices

Sample	Oil Per Cent. v/w	n^{20}_{D} of oil
Coriander fruit	0·34	1·4632
Ground ginger	1·04	1·4966
Nutmeg	5·12	1·4809
Cinnamon	0·48	—
Cloves	15·40	—
Caraway	4·33	1·4898
Juniper berries	0·19	1·4876
Cardamoms (entire)	4·72	1·4650
Cardamoms seeds	3·28	1·4616
Anise fruits (Pimpinella)	2·34	1·5544
Fennel fruits	1·64	1·5472
Cummin fruits	3·14	1·5034

The volatile ether extracts were:

	Per Cent. w/w
Coriander fruit	0·37
Ground ginger	0·99
Nutmeg	5·00
Cinnamon	0·47
Caraway	4·18

A definite weight of the caraway oil was used for a determination of the carvone present by the hydroxylamine method, the proportion found being 60 per cent.

The oils from the cardamoms (Malabar variety) were used for cineole determination by the cresol method, and the two results obtained indicated the presence of 28 per cent. and 24·3 per cent. of that constituent.

The above figures are an indication of the useful particulars to be obtained by means of the apparatus. In the case of dried herbs, they afford several instances where the samples are not satisfactory and, with the drugs and spices, they give indications which will be useful guides to the limits which may be proposed, if such products are ever the subjects of "standardisation."

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Notes

The Editor wishes to point out that the pages of the Journal are open for the inclusion of short notes dealing with analytical practice and kindred matters. Such notes are submitted to the Publication Committee in the usual manner.

THE COLORIMETRIC DETERMINATION OF TRIARYL CARBINOLS

Recently, Morton and Peakes (*Ind. Eng. Chem., Anal. Ed.*, **1933, 5,** 185) described a qualitative micro-test for the presence of triaryl carbinols, which was based on the conversion of the substance, first into the corresponding chloromethane by the action of acetyl chloride, and then into the highly-coloured free radical by reduction with finely-divided silver. Apart from the manipulative difficulties, the extension of this method to the quantitative determination of these derivatives appears to be precluded on account of the peculiar properties not only of the carbinols themselves, but also of the free radicals, which constitute the most reactive entities of the triarylmethyl series.

As Gomberg has shown, the formation of triarylchloromethane through the interaction of acetyl chloride and the carbinol takes place in virtue of two separate processes, the chloromethane being actually produced through the action of acetyl chloride on the triarylmethyl acetate. Actually, therefore, the amount of chloride produced depends on the reactivity of the acetate, and many instances might be cited in which the completion of this reaction is attained only with great difficulty. Moreover, highly basic carbinols, such as the polymethoxylated triphenyl derivatives, yield deeply coloured acetates, and the free radical test is rendered inapplicable for this reason. Even in those cases where the carbinol is converted smoothly into the chloromethane the exclusion of moisture is essential, owing to the extreme ease with which the chloromethane is hydrolysed and to the pseudo-catalytic isomerisation of the radical to colourless derivatives by traces of acids.

At various times we have had occasion to test for the presence of small amounts of triaryl carbinols in certain mixtures, and have found the following method easy of application and extremely sensitive in many cases:—Briefly, the method is based on the formation of highly coloured addition compounds ("halochromic salts") between triarylchloromethanes and inorganic halides, such as zinc chloride or ferric chloride:

$$R_3C.OH + HCl \rightleftharpoons R_3C.Cl + H_2O$$
$$R_3C.Cl + nZnCl_2 \rightarrow R_3C.Cl.nZnCl_2.$$

These highly coloured derivatives offer the advantage that they are stable in the presence of excess acid and are unaffected by oxygen.

A known weight (0·01–0·001 grm.) of the halogen-free material is dissolved in 10 ml. of dry benzene, a small lump of anhydrous calcium chloride added, and dry hydrogen chloride passed through the solution for 15 minutes. After standing for 10 minutes, 5 ml. of the solution are withdrawn and treated with 1 ml. of a saturated solution of zinc chloride in ether, when the highly coloured addition compound is formed. The colour intensity may be compared with that of a standard solution in a colorimeter tube provided with a rubber cap in communication with a calcium chloride tube to prevent intrusion of moisture. For ordinary purposes, however, it is sufficient to add dry benzene from a burette to the coloured solution contained in a flask (provided with a side-tube attached to a calcium chloride tube) until a colour match is obtained with a standard solution.

Incidentally, it may be noted that no colour is produced when solutions of benzophenone, benzohydrol or ethyl benzoate are treated successively with hydrogen chloride and zinc chloride.

The limiting sensitivity of the method as applied to benzene solutions of triaryl carbinols is indicated in the following table, which also includes the colour of the halochromic derivatives:

Carbinol	Colour	Sensitivity (Grms. carbinol in 1 ml.)
Triphenyl	Yellow	25×10^{-6}
o-Methoxytriphenyl	Brown	3×10^{-5}
p-Methoxytriphenyl	Yellowish-brown	25×10^{-8}
2, 4′-Dimethoxytriphenyl	Red	1×10^{-7}
3, 3′, 3″-Trimethoxytriphenyl	Ruby red	5×10^{-7}
3, 4, 5, 4′, 4″-Pentamethoxytriphenyl	Red	2×10^{-8}
o-Tolyldiphenyl	Yellow	5×10^{-6}
Diphenylyldiphenyl	Bright red	1×10^{-7}
Diphenylyl-*p*-anisyl-phenyl	Red	3×10^{-8}
α-Naphthyldiphenyl	Olive green	1×10^{-6}
5-Acenaphthyldiphenyl	Green	1×10^{-7}

It is apparent from these results that the sensitivity of the method increases with the complexity of the triaryl carbinol.

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THE DETERIORATION OF SODIUM HYPOCHLORITE SOLUTIONS

In experiments carried out at this Institute on the viability of *M. tuberculosis* in soil, dung, etc. (Maddock, *J. Hyg.*, 1933, **33**, 103), the elimination of contaminating organisms was effected by means of alkaline hypochlorite solutions. The experiments extended over a considerable period, and various stocks of sodium hypochlorite solutions (10 per cent. available chlorine) were periodically analysed for their content of available chlorine. It was observed that there was an appreciable loss of strength with time of storage and, since some samples were examined over periods of 600 to 700 days, valuable data concerning the deterioration of such solutions were collected.

The samples were kept in brown or blue glass bottles at a fairly constant temperature (16 to 18° C.) in a bacteriological laboratory. The available chlorine was determined by the iodimetric method, the thiosulphate being standardised against dichromate solution at each determination. The table gives the results for two samples of sodium hypochlorite solutions which were supposed to contain 10 per cent. of available chlorine when delivered. The rate of the loss in strength of available chlorine was that of a reaction of the first order and the constant K $\left(= \frac{1}{t} \log \frac{a}{a - x}\right.$, where t represents the time of storage in days, a the initial percentage, and $a - x$ the percentage of available chlorine at time t) is also given in the table.

Sample A			Sample B		
Time of storage, days	Available chlorine per cent.	$K \times 10^{-4}$	Time of storage, days	Available chlorine, per cent.	$K \times 10^{-4}$
−75*	10·74	—	−14*	9·65	—
0	9·37	—	0	9·44	—
20	9·05	17·4	32	9·11	(11·0)
33	8·81	18·6	63	8·57	15·3
47	8·53	19·9	107	8·02	15·3
76	8·06	19·8	126	7·83	14·8
98	7·71	19·8	169	7·26	15·5
108	7·58	19·2	273	6·05	16·3
269	5·79	17·9	286	5·91	16·4
697	3·50	14·2	392	5·00	16·2
746	3·40	15·8	568	3·97	15·3
			617	3·69	15·3
Average		18·1	—	—	15·6

* Period between dates of bottling and of the first analysis.

(The fluctuations in the velocity constant are possibly due to variations in the temperatures of storage.)

The date of bottling was marked on the bottle, and the table gives the calculated strength at the time of bottling. Sample A was above, and sample B was below, the guaranteed strength at the time of bottling, and both samples were roughly 6 per cent. below the guaranteed strength at the time of delivery.

The results show that hypochlorite solutions deteriorate to half their strength in, roughly, 390 to 420 days. The reaction-constant shows that approximately 1/600th of the available chlorine is lost per day which, for concentrations near the 10 per cent. level, amounts to a loss of 0·017 of a unit per cent. of available chlorine per day. It is suggested that manufacturers who have to supply hypochlorite of guaranteed strength of available chlorine at a specified time of delivery should allow for the deterioration of their product at the above rate.

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THE DETERMINATION OF BISMUTH IN COPPER

In their recent paper in the Analyst (1934, 395), Colbeck, Craven and Murray have described an accurate, though elaborate, method of determining small quantities of bismuth in copper. They have, unfortunately, also cast doubts on the precipitation method, which is much easier to carry out with limited apparatus. The authors do not give the details of their method of calcium carbonate co-precipitation of bismuth, and they make no reference to the method published by the Fiscal Policy Technical Sub-Committee of the Brass and Copper Industries (ANALYST, 1933, 58, 475), which was commented on by the writer (ANALYST, 1933, 58, 684). In defence of the precipitation method I should like to make the following remarks:—When very small quantities of bismuth are to be determined, the quantity present is below the solubility limit of bismuth hydroxide or carbonate. It is essential, therefore, that there should be adsorption of the bismuth compound on some added insoluble compound. My experience has shown that most precipitated hydroxides or carbonates do not completely adsorb bismuth carbonate from solution. The most satisfactory one that I have found is iron hydroxide.

Using an especially purified copper and adding iron as a co-precipitant, I have obtained substantially accurate results on known added amounts of bismuth with as little as 0·00001 grm., which, on the 10 grms. of copper taken, represents 0·0001 per cent. The limit of accuracy appears to be determined by the delicacy of the colorimetric determination rather than the efficacy of the precipitation. Four samples of electrolytic copper examined by me by this method contained from 0·0011 to 0·0035 per cent. of bismuth.

Perhaps Messrs. Colbeck, Craven and Murray would compare the iron co-precipitation method with their method, using remelted bismuth-free copper, to substantiate the accuracy of this co-precipitation method.

I should like to point out again the unsuitability of sulphur dioxide for the colorimetric determination of bismuth. The presence of nitric acid is also open to objection.

I have to thank Sir Robert Robertson, K.B.E., F.R.S., for permission to publish this note.

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THE MICROCHEMICAL IDENTIFICATION OF INK IN HANDWRITING

IN forgery cases the identification of the ink with which particular writing has been made is often of considerable importance, and the following method has proved useful as a means of differentiating between inks of similar character. A small pipette, with a capillary end less in external diameter than the breadth of the stroke under examination, is slightly charged by placing the tip in contact with the surface of the reagent, and a minute drop is placed upon the ink-stroke by pressing the pipette tip gently into contact with it. The drop is immediately covered with a small watch glass to prevent evaporation, and allowed to remain one or two minutes; meanwhile the pipette is completely emptied, and is then applied to the drop, which is thus withdrawn from the ink-stroke. The drop is then gently expelled on to a glass slip and allowed to evaporate, the dry (unless glycerol is present) residue being examined under the microscope and photographed.

The reagent used may be water or dilute solutions of volatile acids or ammonia, but the most generally useful one is 1 per cent. acetic acid solution, this usually having little effect upon the oxidised iron-tannin compound or the dye which has been mordanted by it.

The form and arrangement of the crystals of salts, acids, etc., present in the dry residue are characteristic of a particular brand of ink, and, notwithstanding the minute amount of material present, further differentiation is sometimes possible by determination of the approximate refractive index, for which purpose the immersion method with various standard liquids is used.

The residue, after optical examination, may be re-dissolved in water or dilute acid and divided into several portions. By suitable microchemical reactions it is possible to identify aluminium, copper, chromium, sulphates, chlorides, oxalic and salicylic acids, and glycerol.

It is advisable in all cases to make similar blank tests on the paper of the document free from writing, since some of the substances detected may be derived from this source.

If comparison is to be made with unused ink, it is useless to evaporate drops of the original ink and examine the residue. In such cases writing should be done with the known ink with a "ball-pointed" pen and left for a few days to allow the ink to oxidise, after which the test is carried out as described above.

Not only is this method applicable to writing inks, but it often gives valuable information when applied to the aniline dye inks used with rubber stamps, and also with writing made with so-called indelible pencils.

As soon as a test is completed a detailed note of the exact position where it was applied should be made, since this information may be required in evidence later, and it is frequently impossible to identify the spot after the lapse of a few hours.

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Notes from the Reports of Public Analysts

The Editor would be glad to receive the Annual or other Reports of Public Analysts containing matter of special interest to the Society. Notes made from such Reports would be submitted to the Publication Committee.

CITY OF BIRMINGHAM

Annual Report of the City Analyst for 1933

Of the 6300 samples submitted, 5291 were taken in connection with the Sale of Food and Drugs Act, and of these, 265 were found to be adulterated.

Cod-liver Oil and Malt Extract.—One of the 5 samples examined did not agree with the standard laid down by the British Pharmacopoeia, which requires that the article shall contain 10 per cent. of oil and 90 per cent. of malt extract. In addition, the malt extract used must contain nitrogen equivalent to not less than 4·5 per cent. of protein. The extract used in the preparation in question contained only 3·4 per cent. of protein, a deficiency of 24 per cent.

The wholesale dealers from whom the retailer obtained his supply were written to and they denied that any offence had been committed and maintained that the malt used was better than B.P. quality. They further stated that, in their opinion, the quality specified by the B.P. would be foreign malt and that it would be prone to crystallisation. In this connection it is interesting to note that the Agricultural Produce (Grading and Marketing) (Malt, Flour and Malt Extract) Regulations, 1929, give definitions of quality for pharmaceutical malt extract produced from barley grown in England and Wales. The amount of protein required by the Regulations is 5 per cent., which appears to dispose of the firm's contention that extract containing 4·5 per cent. of protein is probably foreign. As to crystallisation there seems to be no obvious reason why this should take place. All the other samples of cod-liver oil and malt extract, and of malt extract itself, have agreed with the B.P. standard, and have shown no sign whatever of crystallisation. The firm was cautioned.

VITAMIN BEVERAGE.—The sample consisted of a brown, coarse powder, with an odour resembling cocoa. It was directed to be mixed for use with boiling water or milk. The ingredients were stated to be nuts, malt, etc., vitamins *A*, *B* and *D*. It was also described as rich in vitamins. Analysis showed that about 83 per cent. was sucrose, and the remainder mainly cocoa. Nuts and malt, if present at all, were in very small amounts. No trace of vitamin *A* could be found by the colour test. Judging from the composition of the article, it was almost certain that vitamins *B* and *D*, if present at all, were in extremely minute quantities. The packers were communicated with and acquainted with the results of the analysis. They agreed to discard all their leaflets and to remove all the remarks relating to vitamins. They stated that the firm manufacturing the article for them had not kept to the original formula, and they sent a sample taken from stock alleged to be made for them by another firm presumably to the correct formula. This sample was, however, of substantially the same composition as the original sample. Practically the whole of the claims made for this article were untrue and misleading.

H. H. BAGNALL

CITY OF LEICESTER

REPORT OF THE CITY ANALYST FOR THE YEAR 1933

THE number of samples of food and drugs analysed during the year was 1140, and of these 55 were certified as "not genuine."

ENAMEL WARE.—A batch of samples was taken, and the various vessels were treated with 1 per cent. solutions of citric and tartaric acids. Both solutions dissolved an appreciable quantity of antimony from one of the samples, whereas another sample, which also contained antimony, was not appreciably attacked. Rhubarb cooked in a pie-dish made of the same ware as the first sample was heavily contaminated (100 grms. containing 18 mgrms. of antimony oxide), and the dish was left with a rough etched surface. In an interview, representatives of the firm who had made the enamel ware stated that they had supplied millions of pieces all over the country without complaint. Nevertheless, they reported that they were revising their methods of manufacture, and were discontinuing the use of antimony pigments (*cf.* ANALYST, 1934, 439).

BATH WATERS.—There is considerable difficulty in maintaining the quantity of chlorine at the optimum for chlorination of the water. Below 0·5 part per million a certain number of organisms will thrive; above 1 part per million the chlorine is manifest to all bathers. The occasional complaints of the effects of the chlorine are not always justified.

TALC IN SODA MINT TABLETS.—One sample of soda mints contained 11·6 per cent. of talc, which would be particularly undesirable for anyone taking the tablets as an aid to digestion. Since 16 other samples of soda mints contained no talc, its presence would appear to be unnecessary even for manufacturing purposes. The vendor, who was also the manufacturer, promised to leave it out in future.

F. C. BULLOCK

Alkali, &c., Works

ANNUAL REPORT OF THE CHIEF INSPECTORS FOR THE YEAR 1933*

THE 70th Annual Report of the Chief Inspectors, under the Alkali, &c., Works Regulation Act and the Alkali, &c., Works Order, 1928, to the Minister of Health and to the Department of Health for Scotland, has been presented to both Houses of Parliament. It gives statistics of the number of visits paid by district inspectors, and the results of the 1881 quantitative analyses made of chimney and other gases escaping into the atmosphere during the processes in operation. Several cases have occurred in which the provisions of the Act have been infringed, notably in sulphuric acid works, but satisfactory conditions were speedily restored, and, with one exception, legal proceedings were not necessary. The district reports from inspectors show that there has been a slow, but steady, improvement in chemical industry during the year.

DUST AND SMELL FROM ARTIFICIAL SILK WORKS.—An unusual complaint was received in the summer, alleging the emission of dust from an artificial silk works. The dust was said to be highly deleterious to vegetation in some neighbouring allotments. The works employ the cellulose acetate method, and it was at once suspected that the dust consisted of finely divided sodium acetate, which was emitted, together with steam, from the driers used to reduce the moisture content of this salt. Further investigation left little doubt that some, at all events, of the trouble was due to this cause. The company have taken certain steps, which, however, can only be regarded as temporary palliative means.

Chlorine treatment of the vitiated air from the viscose artificial silk process, to which Dr. Wylam directed attention in the 69th Scottish Report, has been tried at three English works. At two of the works it is reported that, although the intensity of the smell is reduced, it still remains sufficiently noticeable to be objectionable. The proportion of chlorine used has been varied, but with no more marked success. At a third works the chlorine treatment has, according to the company, been a great disappointment, as not the slightest difference in smell could be detected. At this works strenuous endeavours are being made to reduce the offensive nature of the emission, and a number of possible methods are being thoroughly investigated. It is much to be hoped that the outcome of this work will be some definitely satisfactory and practicable solution of this most difficult problem.

SULPHIDE WORKS.—*The selenium light-sensitive detector* for hydrogen sulphide, in use at the British Dyestuffs Corporation's works at Blackley, has been further improved, and is found to answer its purpose very well indeed (*cf.* ANALYST, 1933, **58**, 537).

De-arsenification plants have not been greatly used. It has been found necessary, occasionally, to draw attention to the condition of oxide purifiers used for absorption of excess hydrogen sulphide.

Absorption of Hydrogen Sulphide by Oxide of Iron.—Following the laboratory work of Dr. Carter, outlined in the 69th Report (ANALYST, **1933**, **58**, **537**), Mr. Brookhouse has investigated the thermal effects of the reaction, employing oxide of iron, slaked lime and a mixture of these materials. A general conclusion to be drawn from his work (which is fully described in Appendix IV of the present Report) is that where condensers are not very efficient, and there is consequently possibility of hydrocarbon vapours passing forward, the use of a mixture of lime and iron oxide for purification purposes is not to be recommended. A calorimetric method of measuring the thermal effects of the reaction is described in detail.

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* Report by Dr. A. Damon and Dr. B. Wylam, pp. 46. H.M. Stationery Office, 1934. Price 9d. net.

CARBON DISULPHIDE WORKS.—Research work by Imperial Chemical Industries, Ltd., has shown that, even with air containing carbon disulphide in very low concentrations, considerable risk of ignition at comparatively low temperatures exists.

Several new registrations have been effected in respect of the removal and recovery of carbon disulphide from benzol. The necessity for the removal of this constituent often arises where the strong acid wash has been omitted. There are several methods in use, some of them being of a secret nature. It is not considered profitable to recover the carbon disulphide, which is extracted from the benzol, especially as it usually is in an impure form. The gases evolved during the process are hydrogen sulphide, together with other malodorous sulphur compounds, and standard methods for dealing with them have not yet been formulated. In the meantime, however, no very great difficulty has been experienced in rendering the process inoffensive. It is anticipated that there will be considerable extension of the practice of removing carbon disulphide by one or other of the methods now on trial.

TAR WORKS.—There has been some resumption of an old method for increasing the yield of pitch from tar. The system involves the blowing of a large volume of air through the heated tar. There has been difficulty in dealing with the large volume of vitiated air thus leaving the stills. Several alternative methods are available, but the Department has been anxious to approve one which is *mutually* agreeable, and herein lies the difficulty. Experiments are in hand, but now that the price of pitch has fallen, it is rather doubtful whether the process will be continued.

An explosion occurred in a still at the Silverdale works of the New Northern Quarries Co., Ltd., which, it was thought, had been due to spontaneous ignition of iron sulphide or finely divided carbon adhering to the side of the still, which had been emptied some hours previously. Damage was confined to the still, and there were no casualties.

Complaints of fumes and grit, said to emanate from tar works, were made by the owner of an adjacent nursery. This matter has not yet been satisfactorily cleared up, and is still under investigation. It is, perhaps, scarcely reasonable to expect that nursery gardens will thrive ideally in the immediate vicinity of a chemical works.

Another complaint against a tar works appeared to be due to the running of pitch at too high a temperature. The installation of a recording thermometer in the pitch run-off pipe has been requested. Such an instrument affords a useful check in these cases, and is to be generally recommended.

EXPLOSION IN BISULPHITE WORKS.—There are registered in Scotland eight works for the production of bisulphite, most of which produce calcium bisulphite on a comparatively small scale. In one of the factories, in which sulphurous acid is also produced, there was an alarming and unexpected explosion in June. Sulphur for the production of sulphur dioxide is burned in a current of compressed air within a rectangular cast-iron, water-cooled burner, and it was within this burner while it was not in operation and was quite cold that the explosion occurred. The process had been discontinued for a week, and the inside of the burner had been cleaned and the flaplids had been closed. When one of the hinged flaplids had been raised to an angle of about 45° an explosion took place within the burner, and the workman was rather seriously burned. There was no naked light near the burner, and the man was not smoking. On examination of the burner it was found to contain hydrogen sulphide, and the mechanism of the explosion thus appeared to be as follows:—The burning of sulphur in an iron container would undoubtedly lead to the production of iron sulphide. When the burner was left cold, sulphur dioxide in it would be converted into sulphurous and sulphuric acids in the presence of moist air. These acids, reacting with the iron sulphide, would produce hydrogen sulphide, and there is no doubt that the accident was caused by an explosive mixture of this gas being ignited by a particle of pyrophoric iron sulphide immediately the workman raised the lid of the burner. Precautions have now been taken to prevent a recurrence of such accidents; these include sweeping out the interior of the burner and the pipe system with a current of compressed air before charging, so as to disperse any pockets of inflammable gas.

Home Office

REPORT OF THE SENIOR MEDICAL INSPECTOR OF FACTORIES AND WORKSHOPS FOR 1933*

THE report of Dr. J. C. Bridge, which forms a special section of the Annual Report of the Chief Inspector of Factories and Workshops, deals with the principal cases of industrial disease and poisoning investigated during the year.

"ANILISM."—Notwithstanding the high temperature prevailing throughout the summer there were only twelve cases notified. Of these, four occurred in the manufacture of intermediates, two in the manufacture or use of aniline, two in dyeing with aniline black, two each in working with paratoluidine and paranitroaniline, and one with dichlorobenzene.

Two cases of chronic benzene poisoning (one of which was fatal in 1934) occurred in works in which there was inadequate ventilation. In one of these (the fatal case) the benzene had been used for mixing cellulose lacquers, and in the other case for cleaning lenses. There were two cases of toxic jaundice, due to the use of tetrachloroethane in wool scouring; the use of a less toxic substance, *e.g.* trichloroethylene, is suggested.

BLADDER CANCER IN DYEWORKS.—An enquiry into the working history of persons affected by new growths of the bladder among Huddersfield chemical workers has been carried out during the last two years by Dr. Currie. Since 1900, when the first death was reported, there have been 31 deaths among chemical workers from this cause, as compared with 71 among non-chemical workers. The average age of death among chemical workers is considerably lower than among non-chemical workers. Of the cases of papilloma and cancer of the bladder admitted to the Huddersfield Royal Infirmary, the trade of chemical labourer was the only one giving a number of fatal cases. It is not possible to specify any particular chemical as the cause of the disease, though contact with certain chemicals appears to predominate in the history of the cases investigated—notably aniline, benzidine, α- and β-naphthylamines, and their derivatives. Assuming that contact with these chemicals is a causative factor of the disease, preventive measures lie in removing dust and fumes from the workrooms, and preventing absorption by handling. Of late years very considerable improvements have been effected, and increased attention must be given to such precautions.

TOXICITY OF TRICHLOROETHYLENE.—Notwithstanding the steadily increasing use of trichloroethylene for dry cleaning, only one serious case was reported, although there have doubtless been other persons affected with milder symptoms (headache and giddiness) who have quickly recovered on removal to fresh air. In the case in question the person was not actually in the workroom, but was affected by the vapour discharged at a low level into a passage way. Unconsciousness resulted, but there was complete recovery in three days. No symptoms of any form of chronic intoxication have been observed.

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* H.M. Stationery Office, 1934. Price 2s. net.

CADMIUM POISONING CASES.—A case of cadmium poisoning occurred in a factory where a man was given 10 lb. of turnings to melt down. He thought that they were composed of silver, but actually they came from cadmium-plated articles and consisted of approximately 92 per cent. of silver and 8 per cent. of cadmium. The melting, which was done in a gas-heated crucible, took about an hour, and for at least half of that time fumes were being given off into a small room, from which there was no adequate of means removing them. About an hour later the man was attacked by coughing, and the cough continued for three days; other symptoms developed later, but recovery was complete in three weeks.

In another case a woman who was engaged during the week in pressing cadmium oxide into containers, during the course of which work a considerable quantity of the oxide was spilt round the press, felt no ill-effects until after sweeping up the dust at the week-ends, when she was constantly affected by nausea and sometimes by diarrhoea.

DERMATITIS CASES.—During the year there were 988 voluntarily reported cases of dermatitis, 18 of which were non-industrial and wrongly diagnosed. At least a quarter of the cases were recurrent, and this points to the prevention of the all-important first attack, for it is only too well borne out in practice that after one attack of dermatitis the skin is less able to resist another.

British Guiana

REPORT OF THE GOVERNMENT ANALYST FOR THE YEAR 1933

IN March, 1933, Mr. Kenneth Wallis, B.Sc., A.I.C., became Government Analyst, in succession to Mr. W. Francis, who retired after twelve years' service.

The work undertaken by the Government Analyst's Department includes analyses for various authorities, and in particular for the Inspector General of Police, the Comptroller of Customs, the Government Medical Officer of Health, and the Municipal Medical Officer of Health. The total number of samples examined was 6462, as compared with 6570 in 1932. These included 3815 articles of food and drink and 217 exhibits in police cases.

MILK.—Of the 3277 samples of fresh milk being hawked by vendors and in process of delivery, 166 were found to be adulterated. The average percentage of fat in the genuine samples was 4·14 per cent., showing clearly that the standard of 3·25 per cent. laid down by the Sale of Food and Drugs (Consolidation) Ordinance is very fair to the vendor. The examination of milk for dirt and extraneous matter was continued, the Tankard apparatus being used. Of the 103 samples examined, none was reported against, proving that the vendors strain the milk before delivery.

FOODSTUFFS FROM THE CUSTOMS DEPARTMENT.—Products which do not comply with the Food and Drugs (Consolidation) Ordinance are refused entry into the Colony. Of the 251 samples examined, 2 samples of butter were rejected for excessive water and salt.

DUTY ON WINES, ETC.—On importation into the Colony the duty on wines, liqueurs, etc., is based on their proof spirit content, according to whether they contain 26, 30, 35, or 42 per cent. Sparkling wines pay a still higher rate of duty.

Under the Food and Drugs (Consolidation) Ordinance, wine to be sold as such must contain a minimum of 13 and a maximum of 42 per cent. of proof spirit.

The Bitters and Cordials Ordinance provides, among other stipulations, for fermented liquors to be sold as "sweets" if they contain more than 4 and less than 26 per cent. of proof spirit.

AERATED WATERS.—Of the 192 samples examined, 12 were imported and 180 of local origin. The local factories are constantly inspected to see that they comply with the conditions for operating laid down by the Governor in Council. The general standard of cleanliness has greatly improved as a result of the increased number of visits of inspection. The use of saccharin in sweetened aerated waters is prohibited.

TOBACCO.—All of the tobacco which is examined from the Customs Department consists of the "black fat" leaf variety. Manufactured cigars, cigarettes, tobacco, snuff, etc., pay specific rates of duty, and have none of the restrictions which are placed on the leaf variety. The latter must contain less than 38 per cent. of water. Formerly, samples were also examined for their percentage of oil, a maximum of 6 per cent. being allowed, but this is no longer required.

CLASSIFICATION OF PETROLEUM PRODUCTS.—Under the table of Specific Duties of the Customs Duties Ordinance there are four classifications for petroleum products, and on arrival in the Colony samples are submitted to determine their classification for the duty to be assessed, and also for storage under the Petroleum Ordinance. Of the 854 samples received, 289 were classified as of the petrol naphtha, benzine type, 386 were paraffin oils (kerosene), 178 were intermediates of the gas, solar, Diesel oil variety, and one was a crude or heavy oil for use in road repairs.

HYDROMETERS AND POLARISCOPES.—The Department is responsible for the custody of reference spirit hydrometers. Spirit shops, sugar estates, and others dealing in spirits, have to submit their instruments at least once a year under the Spirits Ordinance for their accuracy to be tested, for which a small fee is charged. The instruments of other Government Departments are also submitted and tested free of charge. Seventy-three of these instruments were tested during the year.

Clove Produce Inspection

LEGISLATION in Zanzibar (1929) prohibited the export of cloves:

(a) Containing more than 5 per cent. of extraneous matter—clove stems, mother of cloves, twigs, earth, sand;
(b) Adulterated or dyed;
(c) Containing more than 16 per cent. of moisture, as determined by the Brown-Duval tester.

The Zanzibar Clove Growers' Association has issued some explanatory notes on the system of inspection.* Samples averaging 200 grms. in weight are drawn from every second bale in a consignment and placed in trays in front of the bales. The inspector judges by touch whether the moisture-content exceeds 16 per cent., and also estimates whether the extraneous matter exceeds 5 per cent. Cloves containing more than 16 per cent. of moisture feel cold when pressed in the hand, and, when damp, bend, instead of showing a clean break. The method is not altogether trustworthy, for old cloves may appear to be excessively damp (age is indicated by smell and appearance) owing to a redistribution of the oil in the bud after a prolonged period of storage.

If a consignment shows excessive moisture or extraneous matter, the trays are collected and a composite sample is taken. This sample, which averages about 8 lb. from each fifty bales, is carefully mixed on a table, then made into a cone, flattened down to an even plane, and quartered. This procedure is repeated until the composite sample is reduced to two opposite samples of approximately 100 grms. each, forming the final sample (200 grms.) for the laboratory tests.

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* *Pharm. J.*, **1934**, **133**, **42**.

For the determination of extraneous matter, 100 grms. are carefully picked over, and the separated stems, stones, twigs, mother of cloves, and other foreign matter are weighed. If their amount exceeds 5 per cent. the consignment is not passed for export.

For the determination of moisture two 50-grm. samples are taken. If the moisture is considered to be unduly high, only one confirmatory test is made; doubtful consignments are tested twice.

The process consists in putting 50 grms. of the cloves in the Brown-Duvel flask,* adding 75 ml. of heavy motor oil, and heating the flask to 190° C. within a period of 30 minutes, the moisture being collected in a 20-ml. graduated cylinder. At 190° C. the flame is removed, and the flask is allowed to cool to 100° C.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs Analysis

Proteolysis in Stored Eggs. A. K. Balls and T. L. Swenson. (*Ind. Eng. Chem.*, 1934, **26**, 570–572.)—Eggs during storage undergo the two visible changes of a weakening of the membranes round the yoke and a decrease in the proportions of thick to thin white. The changes are shown to be due to the catalytic action of the proteolytic enzyme, tryptic proteinase. This enzyme is apparently confined to the thick white, whilst the thin white contains an inhibiting substance. Either the egg mucin is broken down considerably, or it is hydrolysed sufficiently to form products of a less hydrophylic type, liberating water previously bound to the mucin. Proteolytic activity of the thick and thin white was measured after incubating the diluted white alone and mixed with enterokinase, adding casein and buffer solution, and using the alcoholic titration method of Willstätter and Waldschmidt-Leitz (*Ber.*, 1921, **54**, 2988). Changes in activity were found to vary with time, the activity diminishing practically to vanishing point with fresh eggs, and less quickly with stored eggs. The inhibiting effect of thin white on casein hydrolysis was studied, and the behaviour of thick white towards pancreas extracts, and pancreas proteinase, alone and with kinase. Enzymic action on unwashed thick white under toluene, and the effect of injecting enzyme solution into eggs, were also studied. D. G. H.

Determination of Rancidity in Flours, Semolinas, and Italian Pastes. J. Berlie. (*Ann. Falsific.*, 1934, **27**, 277–279.)—To determine the degree of rancidity in farinaceous foods 5 grms. of the powdered material are extracted with

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* This apparatus was invented by J. W. T. Duvel and Edgar Brown, U.S. Department of Agriculture, Public Service Patent, No. 848616. It is described in U.S. Bureau of Plant Industry Circular No. 72, under the title "A moisture tester for grain and other substances and how to use it."

40 ml. of a mixture of 30 ml. of alcohol, 30 ml. of ether, and 40 ml. of chloroform. To the fatty matter are then added 5 ml. of pure acetic acid, 5 ml. of an alcoholic solution of 5 grms. of potassium iodide in 200 ml. of 95 per cent. alcohol, and 50 ml. of water. The mixture is shaken and left in the dark in a stoppered flask for 24 hours. It is then transferred to another flask, 50 ml. of water being used for rinsing, and titrated in the presence of starch with 0·02 or 0·002 *N* sodium thiosulphate solution, according to the colour obtained. The degree of rancidity is taken as the number of ml. of 0·02 *N* thiosulphate solution used for 100 grms. of material, and the rancidity-index as the degree of rancidity multiplied by 0·00254, and divided by the proportion of fat in 100 grms. As a result of a large number of extractions, rancidity is regarded as present if the rancidity-index reaches 0·1, and as incipient if the index is as high as 0·08. D. G. H.

Detection of Methylene Blue in Flours. P. Nottin. (*Ann. Falsific.*, 1934, **27**, 215.)—In testing for methylene blue in a flour, 20 grms. of the sample are extracted with ether to remove the fat and yellow colouring matters, the ether is allowed to evaporate in the air, and the residue is extracted with 95 per cent alcohol in a continuous-extraction apparatus. The nitrogenous substances adhere sufficiently to the flask to allow of the decantation of the coloured alcohol and of washing with cold alcohol, and the alcoholic solution is then evaporated nearly to dryness. A nitrogenous deposit again remains, and this is washed with 1 ml. of cold alcohol. If methylene blue was present in the flour, the solution is blue-green, and practically the whole of the colouring matter can be made to pass to a piece of filter paper, so that a comparison of colours is easy. D. G. H.

Amount and Determination of Amines in Brandy. K. R. Dietrich. (*Ann. Brass. Dist.*, 1934, **32**, 103; *J. Inst. Brewing*, 1934, **40**, 251.)—A mixture of 250 ml. of brandy and 20 ml. of 10 per cent. sulphuric acid is evaporated with a little pumice in a 500-ml. Kjeldahl flask, and when the liquid is yellow-brown in colour it is cooled and diluted with distilled water free from carbon dioxide. A cork containing two tubes, leading respectively to a tap-funnel and a bulb-condenser, is inserted, and a 33 per cent. solution of sodium carbonate is carefully added through the former until an excess is present. The mixture is then distilled with the condenser-outlet dipping below the surface of a measured quantity of 0·01 *N* hydrochloric acid until about 100 ml. have been obtained and the subsequent distillate is free from alkalinity. The excess of acid is titrated with 0·01 *N* sodium carbonate solution, with methyl red as indicator, in order to obtain the acid combined with the amines plus any ammonia present. Brandy may contain 2 to 15 mgrms. per litre of amines, as methylamine. J. G.

Determination of Iso-propyl Alcohol in Alcoholic Beverages. E. Alessandrini. (*Ann. Brass. Dist.*, 1934, **32**, 104 ; *J. Inst. Brewing*, 1934, **40**, 250–251.) If pyridine is present (as indicated by the white crystalline precipitate produced on distilling the sample and shaking the first 3 ml. of the distillate with a few drops of a saturated solution of anhydrous cadmium chloride in alcohol) 100 ml. of sample are distilled with 1 grm. of magnesia and a little pumice, the distillate (about 65 ml.) being diluted to 100 ml. with absolute alcohol. A mixture of 20 ml. of this solution and 5 ml. of the cadmium chloride reagent is diluted to 50 ml. with absolute alcohol, and after a few hours the liquid is filtered, and 5 ml. of the filtrate are diluted to 100 ml. with water (A). In the absence of pyridine, 5 ml. (or 10 ml. for samples containing less than 40 per cent. of alcohol by volume) of the sample are diluted to 100 ml. (B). In both cases acetone should be absent. *Qualitative.*—A mixture of 3 ml. of A or B with 9 ml. of water and 1 grm. of chromic acid is distilled, and from 2 to 3 ml. of the distillate and 1 ml. of 10 per cent. ammonia are placed in a stoppered container for 3 hours, after which 1 ml. each of 10 per cent. sodium carbonate solution and 2·5 per cent. sodium nitroprusside solution (prepared in the cold) is added; any acetone produced from the *iso*propyl alcohol gives a red colour, turning violet on addition of hydrochloric acid. *Quantitative.*—To the sample (25 ml. of A or B) are added 50 ml. of a 9·6 per cent. solution of potassium chromate (? dichromate) and 100 ml. of 50 per cent. (weight/volume) sulphuric acid; the mixture is cooled rapidly, and after 4 hours 30 ml. of a 25 per cent. solution of ferrous sulphate are added, and the mixture is steam-distilled, 75 ml. of distillate being collected in a receiver immersed in cold water and containing 5 ml. of a 10 per cent. solution of sodium carbonate and 15 ml. of water. This solution is then re-distilled with some pumice, and 50 ml. of the new distillate are collected in a solution of 2 grms. of hydroxylamine hydrochloride in 20 ml. of water. After 1 hour the hydrochloric acid liberated is titrated with 0·1 *N* sodium carbonate solution in the presence of methyl orange, the amount of a blank titration of 2 grms. of hydroxylamine hydrochloride with the sodium carbonate being deducted from the result. The factors for converting the corrected titration figure into grms. of *iso*propyl alcohol per 100 ml. of sample are 0·608 (5 ml. sample, for solution A), and 1·52 (solution B), respectively. J. G.

Metals and Wines. H. E. Searle, F. L. La Que and R. H. Dohrow. (*Ind. Eng. Chem.*, 1934, **26**, 617–627.)—The resistance of metals to wines was studied by exposing specimens of seven metals to wines in process of commercial manufacture; 403 corrosion tests were made. The tolerance of wines for metals was studied by adding citrates of the metals to three wines, and noting the changes; over 125 tests were made. The wines used were a dry white wine (Sauterne), a sweet red wine (port), and a dry red wine (claret); all of these wines had been aged, conditioned and filtered by the usual methods, and all were brilliantly clear before introduction of the citrates. The corrosion tests afforded data for estimating the probable amount of contamination, and these were considered in conjunction with the tolerance tests. The conclusions drawn from the combined tests are that inconel (Ni, 80; Fe, 6; Cr, 13 per cent.) is adequate for all the usual manufacturing processes, and that nickel, monel metal, 18–8 alloy (Ni, 8; iron, 74; Cr, 18 per cent.), aluminium and copper are useful in certain equipment. Iron, tin and tinned metal are of only limited applicability. Metals affect the brilliance or the colour of wines before any changes of flavour or bouquet are noticeable. Only small quantities (3 mgrms. per litre) of iron or tin are required to affect the brilliance; copper in much larger quantities (over 60 mgrms. per litre) has a slight effect on the brilliance of red wines. None of the other metals tested affects the brilliance. Aluminium, copper and chromium have only a slight effect on the colour, and nickel and zinc hardly any. It should be reasonably safe to say that the colour, brilliance, flavour, or bouquet of wines will not be noticeably affected until the metal concentrations exceeds the following limits in mgrms. per litre:—iron, 1; tin, 1; chromium, 15; copper, 60; aluminium, 100; zinc, 200; and monel metal, 200. The paper concludes with a list of references containing 22 entries.

Fat of Camel Milk. O. Laxa. (*Ann. Falsific.*, 1934, **27**, 282–285.)—The fat of camel milk is of a clear yellow colour and pleasant odour. It readily solidifies, and then has a crystalline structure. The analytical figures given were obtained from four separate samples, the first two being mixed. M.pt., 30 to 40° C.; solidification point, 23° to 30° C.; refractometer reading at 40° C., 49·5; saponification value, 196·8; iodine value, 44·5; Reichert–Meissl value, 1·5; Polenske value, 0·9; Hehner value, 94·3. *Fatty acids:* Iodine value, 44·5; refractometer reading at 40° C., 33·5; mol. equivalent, 284·3. The small proportion of volatile acids is noteworthy, particularly as the camel is a herbivorous and ruminant animal. The liquid and solid acids were separated as ammonium salts by David's method (*Compt. rend.*, 1910, **151**, 756). The liquid fatty acids had the molecular equivalent 285 and contained oleic acid. The solid fatty acids melted at 49° to 50° C., and had the molecular equivalent 276; stearic acid was absent. D. G. H.

Fatty Acids and Glycerides of Solid Seed Fats. II. Composition of some Malayan Vegetable Fats. T. P. Hilditch and W. J. Stainsby. (*J. Soc. Chem. Ind.*, 1934, **53**, 197–203T.)—The following Malayan fats have been examined in pursuance of the work relating component fatty acids to botanical families, and also with regard to their characteristic mixed glyceride structure (ANALYST, 1932, **57**, 113). *Sterculia foetida* (*Sterculiaceae*).—The fruits consisted of 23 per cent. of kernel and 77 per cent. of fruit-flesh. *Kernal fat.*—A preliminary treatment of the seed with acetone was necessary in order to remove about 7 per cent. of a dark green resinous material, after which 14 per cent. of fat was readily extracted with petroleum spirit. Abnormal behaviour of the fat on heating did not occur when the resin was first removed. The fat was found to conform in its fatty acids to the general cocoa butter type, and also to follow the usual rule in glyceride structure, the fully-saturated glycerides being insignificant in amount, and the main components of the fat consisting of mixed mono-oleo-disaturated and dioleo-monosaturated glycerides in about the proportions of 57 and 41 per cent., respectively, of the whole fat. The *fruit coat fat* is mainly liquid at ordinary temperatures, and follows the general rule for such fats in having less than 3 per cent. of stearic acid. This is in marked contrast to 40 per cent. in the kernel fat.

Small Siak illipé nuts fat (*Palaquium oblongifolium, Sapotaceae*) resembles the fat of *Allanblackia* or *Pentadesma* more closely than it does Borneo tallow, judging from the analytical figures, but from the composition and glyceride structure the siak fats should be practically equivalent to Borneo tallow as substitutes for cocoa butter. The high content of stearic acid is typical of the seed fats of *Sapotaceae*, so far as these have been studied in detail.

Nephelium sp. (*Sapindaceae*).—The two fats *Nephelium lappaceum* (Rambutan tallow) and *Nephelium mutabile* (Pulasan fat) are characterised by the presence of considerable proportions of *n*-arachidic acid. Rambutan tallow contains almost equal molar proportions of saturated and unsaturated acids and, according to the oxidation experiments, only 1·4 per cent. of fully-saturated glycerides. Pulasan fat is somewhat more saturated, and the relative proportions of stearic and arachidic acids are reversed.

Tonka bean (*Dipteryx odorata*, N.O. *Papilionaceae*).—Expressed and extracted oils gave the following characteristics, respectively:—Saponification value, 192·7, 190·7; iodine value, 76·7, 78·9; unsaponifiable matter, 0·6, 0·4 per cent.; *mixed fatty acids:* Mean molecular weight, 280·6, 283·6; setting point, 41·2° C., 41·2° C. Tonka bean oil resembles arachis oil in composition, but contains between two and three times as much of the higher saturated, C_{20} to C_{24} acids.

All the component acids of the seed fats exhibited the respective qualitative characters already found to be distinctive for their families. On the other hand, the four fats now examined conform closely, irrespective of their plant families, with the general seed-fat rule of "even distribution" of fatty acids through the glyceride molecules.

Fat	Total acids, per cent.							
	Myristic	Palmitic	Stearic	Arachidic	Oleic	Linolic	C_{20} monoethylenic(?)	Unsaponifiable
Sterculia kernel ..	—	10·06	37·85	1·97	40·88	3·13	—	6·11
Sterculia fruit coat ..	—	33·36	2·62	—	58·40	4·07	—	1·55
Palaquium oblongifolium	0·15	5·91	53·68	—	39·65	—	—	0·61
Nephelium, sp. rambutan tallow	—	1·97	13·71	34·50	45·12	—	4·23	0·47
Nephelium, sp. pulasan tallow	—	2·95	30·85	22·18	43·50	—	trace	0·52
Tonka bean								
expressed ..	—	5·10	5·81	$C_{20}C_{24}$ 14·73	60·65	13·15	—	0·56
extracted ..	—	6·09	5·69	,, 13·19	59·35	15·29	—	0·39

D. G. H.

Arsenic-Content of American Cod-liver Oil. A. D. Holmes and R. Remington. (*Ind. Eng. Chem.*, 1934, **26**, 573–574.)—Twenty crude samples of American cod-liver oils from various sources, produced by the "direct-steam method" from absolutely fresh livers, and afterwards filtered, were tested for arsenic. The combustion of the samples was made in the enclosed torch of Kolnitz and Remington (*Ind. Eng. Chem., Anal. Ed.*, 1933, **5**, 38), 5 ml. of oil being used, and the liquid from the absorption bottles and rinsings of the apparatus were combined, acidified with nitric and sulphuric acids, and evaporated until fumes of sulphur trioxide appeared. If darkening occurred, additions of 1 ml. of nitric acid were made until the solution was clear. Arsenic was then determined by the Gutzeit method of the A.O.A.C. Results varied from 1·4 to 5·1 p.p.m. of arsenic, with an average of 2·6 ± 0·13, showing that much more arsenic was present than in vegetables, about the same as in marine vertebrate fish of American waters, but much less than in crustaceans. D. G. H.

Determination of the Proportions of Coffee and Chicory in Coffee Mixtures. E. B. Hughes and W. Wise. (*J. Soc. Chem. Ind.*, 1934, **53**, 189–192T.)—The object of this work was the standardisation of the usual test for estimating the proportions of coffee and chicory in a mixture by measuring the specific gravity of a decoction. The fineness of grinding should be such that the sample passes a 40-mesh sieve; a 5 per cent. extract was found most satisfactory, and half-an-hour was selected as the standard extraction-time. A correction for the water-content of the sample has appreciable importance in allowing for the actual amount of dry coffee or chicory being extracted. The degree of roasting had only very slight effect on the sp.gr. of the extract from coffee, and a satisfactory figure for the sp.gr. (corrected) of 5 per cent. w/v extract of coffee is 1·0058. For chicory, the degree of roasting is important, a rapid and continuous decrease in the soluble content of the product occurring as roasting proceeds, but the figure 1·0143 for the sp.gr. of the 5 per cent. w/v extract, though not so definite as for coffee, has been found satisfactory. For coffee, mean results for 5 per cent. w/v extract give for relation of total solids and sp.gr. (not corrected), total solids = 1·403 per cent. w/v for an extract of sp.gr. at 15·5/15·5° C., 1·0056; whence the specific volume of coffee solids is 0·602 ml. For chicory, total solids = 3·438 per cent. w/v for extract of sp.gr. at 15·5/15·5° C. (not corrected) 1·0137. Whence the specific volume of chicory solids of both coffee extract and chicory extract is the same, and the relation between sp.gr. and total solids for both coffee and chicory extracts can be expressed as: sp.gr. = 1 + 0·004S, where S represents the total solids (per cent.) of the extract (w/v). A table is given of the found and actual compositions of various mixtures, calculated from the expression:

$$\text{Per cent. of coffee} = \frac{(\text{Sp.gr. of chicory—sp.gr. of mixture})}{(\text{Sp.gr. of chicory—sp.gr. of coffee})} \times 100.$$

The apparatus used for preparing the extract consisted of a Pyrex 300-ml. boiling-tube containing a glass bead; in the tube is placed a copper gauze basket (2·5 × 4 cm.) fitted with 3 springs to keep it in place. The 5 grms. of coffee mixture are introduced, and the tube is fixed at a height of rather less than 1 cm. above the surface of the 100 ml. of water, which have been slowly run through the coffee into the tube. The tube and contents are weighed. Heating is adjusted so that the froth on the surface just rises above the top of the basket. No particles of coffee and chicory are thus left on the glass. After boiling, the tube is again weighed and its weight adjusted to the original value if necessary, and the usual procedure of filtering and determining the sp.gr. is then followed. D. G. H.

Detection and Determination of Novocaine and Stovaine. J. A. Sanchez. (*Ann. Chim. anal.*, 1934, **16**, 249–252.)—If a saturated aqueous solution of furfural is acidified by adding 5 drops of acetic acid to 10 ml. of solution, and a drop of this reagent is added to novocaine crystals, an eosin-red colour results. The reaction is negative with stovaine and cocaine. Novocaine, the hydrochloride of *p*-aminobenzoyl-diethylamino-ethanol, in a dilute alcohol solution of a particular strength, behaves as if it were a monobasic acid, and may be determined by titration with alkali hydroxide (phenolphthalein as indicator), whilst the remaining *p*-aminobenzoyldiethyl-amino-ethanol base may then be titrated with standard acid, with rosolic acid as indicator. Similarly, stovaine, the hydrochloride of benzoyl-dimethylamino-*iso*-pentanol, behaves as an acid towards phenolphthalein, and if, after neutralisation, rosolic acid is added as indicator, the liberated base, benzoyl-dimethylamino-*iso*-penthanol may, in turn, be titrated with an acid. To determine the purity of novocaine, 0·1 grm. is placed in a flask, 10 ml. of water and 15 ml. of 96 per cent. of alcohol are added; the mixture is shaken until solution is complete, and 5 drops of phenolphthalein solution are then added. The acidity is titrated by means of 0·1 *N* sodium hydroxide solution; 5 drops of a 20 per cent. alcoholic solution of rosolic acid are then added, and the alkalinity of the liberated organic base is determined with 0·1 *N* sulphuric acid (to the point of production of a golden-yellow colour when viewed against a white background). If the novocaine is pure, the volumes of acid and alkali used will be the same. To find the proportion of novocaine in the solution, the number of ml. used in the two titrations is multiplied by the factor 0·02725 to give the weight of novocaine in the 0·1 grm. taken for the determination.

For stovaine the procedure is similar up to the point of the addition of rosolic acid, and titration of the free base with 0·1 *N* sulphuric acid. In order to find the end-point, the solution is divided into two equal portions, and acid is added to one until there appears to be no further change of colour. The same number of drops of acid are then added to the second portion, followed, at once, by one further drop, and, after shaking, the tints of the two solutions are compared, this procedure being repeated until no further change is visible. The type of tint is thus determined, and a second determination is then made without dividing the solution. The factor required is 0·02715. D. G. H.

Senna Stalk, its Anatomy and Detection in Powdered Senna. A. H. Saber. (*Pharm. J.*, 1934, **133**, 73.)—In the B.P. 1932 monograph on senna leaves the term "stalks" includes portions of the rachis, petiole and stem of the senna plant. The anatomical details of the three parts are almost identical, and the presence of stalk in the powdered leaf may be detected by (*a*) the presence of simple starch grains having a diameter exceeding 6·5 μ, and also compound grains; (*b*) the absence of lignified sclerenchymatous cells; and (*c*) the lignified, thin-walled, simple pitted cells of the pith. S. G. S.

Determination of Senna Stalk in Senna. A. H. Saber. (*Pharm. J.*, 1934, **133**, 74). The epidermal area per grm. of powder (No. 85 mesh) is estimated microscopically after clearing with 5 per cent. potassium hydroxide solution. The count is compared with that obtained for a genuine sample, and from it the percentage of "stalks" can be calculated. (See also *Quart. J. Pharm.*, 1934, **7**, 161.) The method is preferred to the determination of crude fibre, but is not trustworthy with less than 5 per cent. of stalk. S. G. S.

Note on the Sulphuric Acid Test for Liquid Paraffin. C. H. Hampshire and G. R. Page. (*Pharm. J.*, 1934, **133**, 65.)—The wording of the B.P. test is criticised as being too vague, and the colour standard (pale brown) is difficult to define. The U.S. Treasury definition of "pale amber" is similarly criticised. The following alternative test is suggested:—A glass-stoppered test-tube (120 mm. long and 20 mm. internal diameter) is rinsed out with the reagent (nitrogen-free sulphuric acid; 96 per cent. by weight of H_2SO_4) and allowed to drain. Five ml. of the sample and 5 ml. of the reagent are then placed in the tube and shaken vigorously for five seconds. The stopper is loosened, and the tube is placed in a boiling water-bath and heated for ten minutes. At the end of the second, fourth, sixth, and eighth minute the tube is removed from the bath and shaken vigorously for five seconds. After ten minutes the mixture is transferred to a small dry separating funnel, having an ungreased tap, and allowed to stand for ten minutes. The lower layer is then run off into a 1-cm. glass Lovibond cell, and the colour is matched against standard Lovibond glasses. The colour should not exceed 2·5 red and 6·5 yellow. The suggested test for nitric acid in the sulphuric acid is to dilute 45 ml. of the acid with 5 ml. of water, cool the mixture, and add 8 mgrms. of diphenylbenzidine; the solution should remain colourless or become not more than pale blue. S. G. S.

Determination of Elemental Sulphur. H. R. Fleck and A. M. Ward. (*Quart. J. Pharm.*, 1934, **7**, 179–181.)—The weighed material, containing preferably about 0·1 grm. of sulphur, is boiled beneath a reflux condenser with 2 grms. of crystalline sodium sulphite (Na_2SO_3, $7H_2O$) and 30 to 40 ml. of water until the sulphur has dissolved, having been quantitatively converted into sodium thiosulphate. The addition of 1 grm. of soft paraffin wax, as recommended by Allport (*Quart. J. Pharm.*, 1933, **6**, 431), accelerates the reaction. After complete solution of the sulphur the liquid is cooled and decanted from the paraffin, which is then twice extracted with small quantities of hot water and cooled, the washings being added to the main solution. The excess of sulphite is then rendered inactive to iodine by adding 10 ml. of 40 per cent. formalin and 10 ml. of 20 per cent. acetic acid (Kurtenacker and Bittner, *Z. anorg. Chem.*, 1925, **142**, 115), and the solution is diluted to 150 ml. and titrated with $N/10$ iodine solution (starch as indicator). The blue end-point fades slowly, possibly owing to slow interaction of the iodine with the formaldehyde-bisulphite compound; 1 ml. of $N/10$ iodine $\equiv$ 3·206 mgrms. of sulphur. The method is applicable to the determination of sulphur in flowers of sulphur, sulphur ointment, confection of sulphur, sulphur tablets and liquorice "compounds."

Determination of Tin in Organic Material, with Special Reference to Canned Foods. G. Lunde and E. Mathieson. (*J. Soc. Chem. Ind.*, 1934, **53**, 203–204T.)—The method recommended for determining tin in canned foods is a modification of Owe's method (*Svensk Kem. Tidsskr.*, 1924, **36**, 5). Thirty to 60 grms. of the sample are placed in a Kjeldahl flask with 25 ml. of concentrated sulphuric acid and 50 ml. of water, together with a few glass beads, and the liquid is heated until white fumes are evolved. Concentrated nitric acid (96 per cent. redistilled) is added in portions of about 10 ml., and heating is continued till the organic matter is destroyed. If a large proportion of fat is present, it is first removed either by adding 50 ml. of toluene to the sample, and 25 ml. of concentrated sulphuric acid (20 to 30 ml. of water being first added if required), shaking for 30 minutes and removing the toluene layer by centrifuging; or by heating the sample slowly with 25 ml. of water and 25 ml. of concentrated sulphuric acid until the fat and protein are partly hydrolysed, and then separating the fat layer while still hot, in a funnel, and proceeding with the remainder in a Kjeldahl flask. After destruction of the organic matter the remaining nitrogen compounds are removed by adding 25 ml. of saturated ammonium oxalate solution, heating until sulphur trioxide fumes are evolved, and repeating the operation with a further 10 ml. of oxalate solution. The solution is transferred to a washing-bottle with a ground-glass stopper, 60 ml. of water and 50 ml. of concentrated hydrochloric acid are added, and the solution is reduced by heating with 0·3 to 0·4 grms. of granulated aluminium (Merck) in a rapid current of carbon dioxide, after which the separated metallic tin is dissolved by bringing the liquid just to boiling-point. The flask is then cooled to 10 to 15° C., the stream of carbon dioxide being maintained; 25 ml. of 0·02 *N* iodine are added, and the liquid is diluted with water and titrated at once with 0·02 *N* sodium thiosulphate solution. The iodine solution is standardised against metallic tin dissolved in concentrated hydrochloric acid.

D. G. H.

Biochemical

Determination of Bromine in Normal Blood. T. F. Dixon. (*Biochem. J.*, 1934, **28**, 48–51.)—A method is described for the determination of the bromine-content of 10 ml. of normal blood, whether it contains 0·1 mgrm. or 100 mgrms. per 100 ml. According to van der Meulen (*Chem. Weekblad.*, 1931, **28**, 82) bromides can be quantitatively oxidised to bromates by addition of 2½ times the theoretical amount of hypochlorite in the presence of borate buffer and half-saturation with sodium chloride, according to the equation $3KClO+KBr \rightleftharpoons KBrO_3+3KCl$. The completion of the reaction from left to right is ensured if the oxidation is carried out at 85° C. and excess hypochlorite is removed by addition of hydrogen peroxide, which in turn is removed by boiling. Addition of bromates to iodides in acid solution results in the liberation of iodine equivalent to 6 times the original amount of bromine, according to the equation $HBrO_3+6HI \rightleftharpoons HBr+3H_2O+3I_2$. The above procedure is modified to deal with quantities of the order of 50γ, such as are likely to be encountered in 10 ml. of normal blood. *Reagents required.*—Water distilled from alkali in an all-glass apparatus. 10 *N* Potassium hydroxide and 10 *N* potassium carbonate solutions purified so as to contain no bromide. Pure ethyl alcohol distilled in all-glass apparatus from potassium hydroxide. *N* Potassium hypochlorite in *N*/10 potassium hydroxide solution, made by passing 71 grms. of chlorine gas, cooled and dried, into 1·8 litres of potassium hydroxide containing 2·2 grm.-mols. or 123·2 grms. of potassium hydroxide, and making up to 2 litres with water. (While the chlorine is passing through the liquid the flask is cooled in ice.) Freshly prepared *N* potassium iodide solution. *N* Hydrochloric acid. A freshly prepared 0·5 per cent. solution of acid-washed soluble starch. *N* Hydrogen peroxide. *N*/500 Sodium thiosulphate solution. *Method.*—Into a 300-ml. flask are measured 10 ml. of oxalated blood, 0·8 ml. of 10 *N* potassium hydroxide solution, 0·8 ml. of 10 *N* potassium carbonate solution, and 30 ml. of water, and the whole is heated on the water-bath for 4 hours. The mixture is transferred to a nickel basin, 10 cm. in diameter, and evaporated to dryness. The basin is dried at 150 to 160° C. for 60 minutes, then heated at 420° C. in the muffle furnace for 2 hours, and finally at 500° C. for 30 minutes. The contents are ground up with water by means of a rod, evaporated to dryness, dried at 150 to 160° C.

for 30 minutes, and then ignited for 30 minutes at 500° C. The grinding with water, drying at 160° C., and igniting at 500° C. for 30 minutes are repeated. During ignition in the muffle the contents of the basin swell up considerably, and to prevent loss the surface of the melt is pricked with a finely-pointed glass rod. Then 20 ml. of water are introduced into the basin, which is heated on the water-bath for a few minutes. The contents are ground up and filtered through a 9-cm. Whatman's No. 5 filter-paper, previously well washed, into a 9-cm. porcelain basin. The residue is repeatedly extracted with hot and, finally, cold water until there are about 50 ml. in the porcelain basin, which is then heated on the water-bath until a dry residue is left. This is dried first at 120° C. for 15 minutes, then at 150 to 160° C. for 15 minutes, and, finally, ignited in the muffle for 10 minutes at 500° C., after which it is dissolved in 15 ml. of water, and the solution is filtered through a 7-cm. Whatman's No. 42 filter-paper into another porcelain basin, the filter being washed several times with $N/10$ potassium carbonate solution. The filtrate and washings are evaporated on the water-bath, and the residue is dried at 150 to 160° C. and ignited in the muffle for 5 minutes at 500° C. It is then dissolved in 1·8 ml. of water, and alcohol is added, 5 ml. at a time, with continuous stirring, the mixture being well rubbed with a rod until 15 ml. of alcohol have been added. The mixture is stirred until the potassium carbonate passes into a pasty condition, after which the alcoholic layer is decanted through a No. 3 Jena glass sintered filter, into a 30- or 40-ml. flask. The residue is extracted with two more successive portions of 5 ml. of alcohol. To the potassium carbonate, from which the alcohol has been drained, is then added 0·6 ml. water, and the extraction with alcohol is repeated. The contents of the flask are evaporated on the water-bath to dryness, and the last traces of alcohol are removed by heating at 150 to 160° C. for 10 minutes. To the residue are added 2 ml. of water, 1 ml. of potassium hypochlorite solution and 2·5 ml. of saturated sodium chloride solution, and the mixture is warmed to about 85° C. on the water-bath and treated with 1 ml. of saturated boric acid solution. The flask is removed after 20 minutes and cooled, 1 ml. of N hydrogen peroxide is added, and the mixture is gently boiled for 5 minutes. The flask is again cooled, and 1·5 ml. N hydrochloric acid, 5 drops of starch, and 1 ml. of N potassium iodide solution are added, and the solution is titrated against $N/500$ thiosulphate solution, a 3- or 5-ml. micro-burette being used. One ml. $N/500 \equiv$ 26·7γ of bromine. The oxidation of the bromide in the presence of chloride is conveniently carried out in the same flask as the titration. P. H. P.

Comparative Zinc-Contents of Green and Etiolated Leaves. G. Bertrand and A. Andreitcheva. (*Bull. Soc. Chim.*, 1934, [5], 1, 406–408.)—Previous work (cf. *id.*, 1929, [4], **45**, 168) has been extended to determination of zinc in leaves of plants which are completely etiolated by the method of culture (*e.g.* endive and nasturtium); to plants whose leaves show varying degrees of green colour (*e.g.* cress, dandelion, sorrel and spinach); and to plants which bear green and etiolated leaves simultaneously (*e.g.* certain salads and cabbage). The determinations were made on 1 kilo. of material by the calcium zincate method (*cf.* G. Bertrand and others, *Compt. rend.*, 1892, **115**, 939, 1028; *Bull. Soc. Chim.*, 1906, [4], **1**, 63; *id.*, 1923, [4], **33**, 1539; ANALYST, 1921, **46**, 244), the metal being weighed as the anhydrous sulphate, and the results confirm those previously indicated, *viz.* that there is a certain degree of parallelism between the zinc-contents of the leaves and the degree of coloration by chlorophyll. Thus, for example, the green and etiolated leaves of lettuce heads contained 119·31 and 50·44 mgrms. of zinc per kilo. of dry material, respectively, the corresponding figures for endive being 105·41 and 33·80, and for cabbage 33·02 and 15·09; leaves of dandelion contained 97·51; cress, 100·56; sorrel, 45·98; nasturtiums, 22·70; and spinach, 66·70 mgrms. per kilo. It is questioned whether zinc and manganese (*cf.* Bertrand and Rosenblatt, *Bull. Soc. Chim.*, 1932, [4], **51**, 862) are concerned in the production of chlorophyll. J. G.

Carotene in Palm Oil. K. Kobayashi, K. Yamamoto, and J. Abe. (*Memoirs of the Faculty of Science and Engineering, Waseda University, Tokyo, Japan,* 1934, **11**, 1–3.)—Palm oil from the Eastern Japanese Archipelago has a peculiar reddish-orange colour, and the following analytical constants:—Sp.gr. at 30° C., 0·9110; acid value, 3·88; saponification value, 213·2; iodine value, 50·33; n_D^{30}, 1·4770. On the addition of strong sulphuric acid or Japanese acid clay the reddish-orange colour changes to bluish-green. This resembles the colour reaction of Japanese acid clay with carotene, cod-liver oil and vitamin *A*, previously reported by these workers (*cf.* Absts., ANALYST, 1927, **52**, 553, 558; 1929, **54**, 562; 1931, **56**, 198; 1932, **57**, 264). This reaction implies that the colour of the palm oil is due to carotene. Confirmation was obtained by comparison of the colour-intensity and solubility of palm oil and of carotene in various solvents. Further support to this conclusion is given by the action of anhydrous aluminium chloride, anhydrous zinc chloride, ferric chloride and phosphorus pentachloride. The absorption spectrum in alcohol and petroleum spirit also shows a similarity between palm oil and pure carotene, and it is concluded that the principal pigment, at least, of this palm oil is carotene. S. G. S.

Colour Reaction of Japanese Acid Clay with Carotene in Palm Oil. K. Kobayashi, K. Yamamoto and J. Abe. (*Memoirs of the Faculty of Science and Engineering, Waseda University, Tokyo, Japan,* 1934, **11**, 4–10.)—The palm oil was from the same source, and had the same constants as that referred to in the previous abstract. It was dissolved in benzene or petroleum spirit to give a 10 per cent. solution, and the clay was dried at 120° C. for three hours. From these solutions the palm oil is adsorbed by fuller's earth, Florida earth, German activated clays and Japanese acid clay, the precipitated clay layer having a bluish-green colour. Kaolins, ordinary clays, silica gels, certain pyrophyllites, loams, kieselguhrs, etc., give a weak colour reaction or none at all. Benzene, petroleum spirit, carbon disulphide, carbon tetrachloride and chloroform all allow the reaction to take place; but with ethers, methyl and ethyl alcohols and acetone no colour is obtained. With such dehydrating or condensing reagents as strong sulphuric acid, anhydrous zinc chloride, anhydrous aluminium chloride, anhydrous ferric chloride, anhydrous antimony trichloride and phosphorus pentoxide, a similar colour is given by carotene, vitamin *A*, and cod-liver oils, but, since carotene is a hydrocarbon, this colour cannot be due to condensation or dehydration. If the substance which has been adsorbed by the coloured acid clay is removed by extraction with alcohol, ether or acetone, the solvent removed under reduced pressure in an atmosphere of carbon dioxide, and the residue dissolved in benzene or petroleum spirit, the addition of fresh acid clay will give the same colour, and the strength of the colour-reaction is maintained after a succession of such treatments. The authors suggest that this is due to the clay adsorbing carotene, and find their conclusions supported by spectroscopic methods. They also suggest that the colour-reaction with the acid clay is due to polymerisation. S. G. S.

Toxicological

Lead Poisoning in Children [Chemical Mechanism of Lead Poisoning]. T. S. Rodgers, J. R. S. Peck and M. H. Jupe. (*Lancet*, 1934, **227**, 129–133.)—The importance of radiography in the diagnosis of lead poisoning in children is illustrated by a case report, and a brief outline is given of the effects of lead on the body. In the case clinically described the poisoning was attributable to the chewing of "tin soldiers," and the radiological changes at the ends of the long bones were significant features. The mechanism of the anaemia associated with plumbism has only recently been elucidated. Lead changes the colloidal state of the cell surface by a deposition of insoluble lead phosphate and a local production of acid; this causes shrinkage and hardening of the cell wall which, while making it more resistant to changes in osmotic pressure, makes the cell more brittle and less sticky. The brittle cells are readily destroyed in the process of circulation, and so a haemolytic anaemia is produced. To this is due the increase of pigment in the blood, bile and urine which is sometimes found. The blue line of the gums is due to a sub-epithelial deposit of lead sulphide. The circulating tertiary lead phosphate is converted locally into the very soluble di-lead salt by slight changes in the reaction of the tissues, and this combines readily with hydrogen sulphide which diffuses through the gums, being formed from the decaying protein of food material left in crevices between the teeth. The lead line is rarely seen when the teeth are kept clean, and is not found in the herbivora. Lead colic is due to the action of the metal on smooth muscle, and the primary changes in lead palsy are also in the muscle. Lead, circulating as insoluble colloidal phosphate, meets the lactic acid of fatigued muscle, and is precipitated on the surface as lead phosphate by reacting with the inorganic buffer phosphate of the cell; this changes the properties of the cell surface and leads to lead palsy. It has long been known that the muscles most used are those most often paralysed.

Aub (*Medicine*, 1925, **4**, 1) has shown that the metabolism of lead and calcium in the body is similar, and the modern treatment of lead poisoning is based upon this fact. Factors favouring the storage of calcium in the bones, such as vitamin *D* and an adequate and balanced phosphorus-calcium intake, will also aid in the deposition of lead, and will therefore be of use in the acute phases of lead poisoning when lead is widely distributed. In latent poisoning, measures which cause an increased excretion of calcium may be used. Acid or acid-forming salts will cause an excretion of lead, which is increased by giving a low calcium diet, and alkalis and potassium iodide have a similar, though less pronounced effect. Magnesium hinders calcification, and, therefore, probably the deposition of lead; it should not be given in cases presenting symptoms of acute poisoning. Lead is excreted mainly by the bowel and, to a less extent, by the kidneys; the gall-bladder is also probably concerned to a slight extent in the excretion. Lead found in the faeces may have passed through the intestinal tract unchanged, but lead found in the urine proves absorption, and is therefore of great diagnostic importance. The paper is illustrated by *X*-ray photographs showing the areas of increased density at the ends of the diaphyses, sometimes called "lead lines," and there is a list of 26 references to the papers on lead poisoning published between 1901 and 1933.

Toxicity Tests with Rhenium. L. C. Hurd, J. K. Colehour and P. P. Cohen. (*Proc. Soc. Exp. Biol. and Med.*, 1933, **30**, 926; *Pharm. J.*, 1934, **132**, 78.)—The lethal dose of manganese for rabbits is 5 to 6 mgrms. per kilo. of body weight (Hanzlik and Sollman), but in experiments with rhenium, the rare congener of manganese, the authors have injected into rats as much as 200 mgrms. per kilo. of body weight without producing any ill effects. Rhenium could be detected spectrographically, half an hour after injection, in the testes, heart, kidney, liver, and spleen, and especially in the urine.

Detection of Chloroform, Carbon Tetrachloride, etc. in Toxicological Cases. Application of the Method to their Detection in Air. Kohn-Abrest. (*Compt. rend.*, 1934, **199**, 237–239.)—For the examination of organs, 25 to 100 grms. of the frozen material are cut up and placed in a 250-ml. flask with an equal volume of water and 1 per cent. of tartaric acid. By means of an aspirator, air is drawn, at the rate of 5 litres per hour, in succession through two wash-bottles containing a 5 per cent. solution of silver nitrate in strong nitric acid; the above flask, heated at 90 to 95° C.; two similar wash-bottles in a bath at 60 to 70° C.; a quartz tube (30 cm. long, 1·4 cm. in diameter), 10 cm. of which are heated in a resistance-furnace at 900° C.; a 10-ml. Liebig bubbler, and, finally, a "guard" wash-bottle, both containing a 5 per cent. solution of silver nitrate in nitric acid. The two wash-bottles after the flask remove hydrogen sulphide, hydrogen cyanide, and hydrochloric and hydrobromic acids, and the alkyl halides decomposed in the hot tube give, after 1 hour or less, a precipitate in the bubbler, the sensitiveness being a few parts per million. For the detection of chloral the distillate from 1 kilo. of viscera may be used, or the viscera are placed in the flask and, after the above procedure, they are made alkaline (to liberate chloroform), and a second determination is carried out after acidification (to detect it); a blank determination is necessary. The apparatus may also be used for the detection of alkyl halogens in air or, if suitable reagents are used, for ordinary gas analyses. J. G.

Poisoning by Vapours of certain Esters used as Solvents. P. Duquenois and P. Revel. (*J. Pharm. Chim.*, 1934, **126**, 590–601.)—The study of the action of methyl formate, ethyl formate, methyl acetate and ethyl acetate vapours on frogs and guinea pigs led to the conclusions that these esters cause a constant diminution in the nerve *chronaxia* and a slight augmentation in that of the muscle. It was found that the poison acted on the nerves before the muscles, and that methyl formate gave rise to the most accentuated effects, the nerve and muscle soon becoming non-excitable, with accompanying rigidity. If large and continued doses are administered, the poison penetrates cutaneously. Prolonged inhalation of these esters is toxic, and, although the methyl esters are regarded as more toxic than the ethyl esters, this is probably due to their lower boiling-point. The methyl esters are tear-producing and cause atrophy of the optic nerve, whilst the ethyl esters are intoxicating. Since these esters are used as solvents for cellulose nitrate and acetate in making varnishes for aeroplane wings, and in the straw-hat and other industries, it would not seem possible to prohibit their use, but precautions against exposure to their vapours should be taken, and special attention should be directed to the ventilation arrangements. D. G. H.

Organic Analysis

Determination of Aliphatic Nitrates by Titration. J. W. H. Oldham. (*J. Soc. Chem. Ind.*, 1934, **53**, 236T).—A solution of 0·1 to 0·4 grm. of the sample in 10 to 15 ml. of hot glacial acetic acid is boiled for 20 minutes with an excess of a 0·1 *N* solution of titanous sulphate, which has previously been reduced by means of liquid zinc amalgam. The hot solution is then back-titrated with a standard solution of ferric alum until a permanent blue or blue-green colour is obtained with methylene blue; the reagents are standardised from time to time against potassium dichromate. Owing, probably, to the escape of nitric oxide, the calculation of the results must be based on the assumption that each nitrate group requires only 7·5 atoms of titanium (instead of 8), and the results obtained for 13 complex carbohydrate nitrates (including 2 in which the nitro-group is present in the aromatic ring of a substituent) show divergencies between the percentages of nitrogen found (3·38 to 14·97 per cent.) and calculated, of +0·31 to −0·15 per cent. The method is not applicable to inorganic nitrates or to nitrates of bases such as carbamide. J. G.

Determination of Butanediol-2.3. C. Matignon, H. Moureu and M. Dodé. (*Bull. Soc. Chim.*, 1934, [5], **1**, 411–419.)—Since butanediol-2.3 plays an important part in fermentation phenomena, it is desirable to be able to determine it, particularly in the presence of butanediol-1.2, and the method suggested is oxidation to acetyl-methyl-carbinol, which is determined in turn, after transformation into diacetyl, as nickel dimethyl-glyoxime (*cf.* Lemoigne, *Compt. rend.*, 1920, **170**, 131; ANALYST, 1930, **55**, 642; A. J. Kluyver, H. J. L. Donker and F. V. Hooft, *Biochem. Z.*, 1925, **161**, 361). Methods of obtaining constant yields in the primary reaction are described and discussed, together with the results of experiments on the effects of variables such as time, temperature, quantity of reagent, etc., and the following procedure is suggested:—A mixture of 30 ml. of the sample, corresponding with 0·1 to 0·2 grm. of butanediol-2.3, and 30 ml. of saturated bromine water, is sealed in a small thick glass flask, which is completely immersed in a water-bath at 100° C. for exactly 3 minutes. The flask is then cooled in the dark and opened, and the excess of bromine is destroyed by addition of the minimum quantity of a 20 per cent. solution of sodium sulphite. The liquid is then distilled in the presence of 15 ml. of ferric chloride solution (45° Bé.), the resulting diacetyl being collected in a solution containing 2 grms. of hydroxylamine hydrochloride, 10 ml. of 20 per cent. sodium acetate solution, and 10 ml. of a 10 per cent. solution of nickel chloride. The distillate, which should amount to about one-half of the original, is allowed to stand overnight, and is then warmed for 1 to 2 hours on the water-bath, after which it is cooled and the precipitate is collected on a sintered-glass crucible, then dried at 110° C. and weighed (*p* grms.). Under the above conditions the yield of the primary reaction is constant (75·6 per cent.), and the weight of butanediol-2.3 is 0·824*p* grms., the maximum error (for 0·14 to 0·165 grm. of butanediol-2.3) being about 1 per cent. Very dilute solutions may be concentrated or determined colorimetrically by working with 5 ml. each of the sample, bromine water and ferric chloride and 10, 20 and 5 drops, respectively, of a 20 per cent. solution of hydroxylamine hydrochloride and of the sodium acetate and nickel chloride solutions. The colour of the nickel dimethyl-glyoxime may then be matched against those produced in the same way from a range of known quantities of pure butanediol-2.3. This is prepared by dehydration of butanol-1 with alumina, followed by conversion into butene and thence into the dibromide and diacetate (using silver acetate as reagent) of this substance; the glycol is then produced by alcoholysis (*cf.* C. Matignon, H. Moureu and M. Dodé, *Compt. rend.*, 1933, **196**, 973), any butanediol-1.2 being removed by distillation in a vacuum. The colorimetric method may be used with an accuracy of 15 to 20 per cent. for solutions containing 0·02 to 0·03 per cent. of butanediol-2.3, and it is also useful as a means of determining the approximate strength of the sample in preparation for the gravimetric method. J. G.

Colour Reaction of Azulenogenic Sesquiterpenes. S. and H. Sabetay. (*Compt. rend.*, 1934, **199**, 313–316.)—Azulenogenic sesquiterpenes are constituents of many essential oils, and may be detected by the blue colour obtained with a solution of bromine in chloroform. The bromine dehydrogenates the sesquiterpene and yields azulene. In applying the test, from 1 to 5 drops of the essential oil (according to its richness in sesquiterpenes) are dissolved in 0·2 to 2 ml. of chloroform and the solution is treated with 0·1 to 1 ml. of a 5 to 10 per cent. solution of bromine in chloroform. After a few minutes a blue, green or violet colour is produced if these sesquiterpenes are present. Certain sesquiterpenic alcohols (*e.g.* guaiol) give a violet colour. Analogous colours are produced by heating the essential oils with sulphur. Among the numerous essential oils which give the reaction with bromine in chloroform are the following:—elecampane, copaiba balsam, guaiacum, cade (freshly distilled), cajuput, chamomile, cubebs, elemi, eucalyptus, galangal, galbanum, juniper, geranium (Bourbon, Moroccan, Spanish, African), ginger, hop, lovage, certain peppermints, yarrow, myrrh, neroli, pimento, black pepper, distilled rose (Bulgaria, Grasse, Algiers), valerian, verbena, ylang-ylang. The azulenogenic terpene, isolated from Bourbon geranium oil by saponification, fixation of the alcohols as borates, and fractional distillation, had the following characteristics:—B.pt., 117 to 120° C.; n_D^{20}, 1·5021; sp.gr. at 15°/15° C., 0·9134; α (1 dm.), +11·40°.* It contained C, 87·98; H, 12·2 per cent. (calculated for $C_{15}H_{24}$:—C, 88·23; H, 11·76 per cent.) This terpene gave a yellow colour with antimony trichloride (indicating a double bond), and an intense blue with bromine in chloroform, or when heated with sulphur, or with a mixture of nitric and acetic acids in the cold. The bromine-chloroform reaction may be adapted to the colorimetric determination of these terpenes, and could probably also be used for the preparation of azulenes.

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* The heating with boric acid probably changed the rotation.

Adulterated Cananga Oil. W. H. Simmons. (*Perf. and Essential Oil Record*, 1934, 25, 167.)—During recent years inferior and adulterated cananga oil has been of much more common occurrence, and fairly light fractions of petroleum oil appear to have been used for adulteration. The ordinary analytical figures in such cases will not disclose even heavy adulteration. The flash-point is useful. A sample considered above suspicion gave a flash-point (by the closed Pensky-Martens test) of 93° C., and two adulterated samples gave values of 82° and 83° C., respectively. A modification of the polymerisation test for turpentine oil was devised and found useful:—Two ml. of oil are measured into a Leffmann-Beam milk-fat flask, which is half filled with concentrated sulphuric acid; the flask is immersed in cold water and shaken for 1 minute; sufficient acid is added to bring the level into the neck of the flask, and after standing overnight the volume of the oily layer is read. The two above-mentioned oils gave residues of 15·5 and 14·2 per cent., respectively, of oil, and another inferior sample 12·5 per cent., whilst satisfactory cananga oils were never found to give more than 5 per cent. Probably the refractive index will give the most definite conclusion as to purity. In the case of the second of the two adulterated oils it was n_D^{20} 1·4700, whilst for the satisfactory oil it was n_D^{20} 1·4919. D. G. H.

Florida Grape-fruit Peel Oil. E. K. Nelson and H. H. Mottern. (*Ind. Eng. Chem.*, 1934, 26, 634–637.)—The essential oil expressed from the peel of Florida grape fruit, and separated from aqueous constituents in a centrifugal separator, consists of approximately 90 per cent. of limonene, 2 to 3 per cent. of oxygen-containing volatile constituents and sesquiterpenes, and 7 to 8 per cent. of wax-like substances. The following other constituents were identified:—Octyl and decyl aldehydes, geraniol and octyl alcohol (both free and as acetates), cadinene, and small quantities of citral and methyl anthranilate. No pinene, terpineol or decyl alcohol was found. There were no pronounced differences in the results given by oil from hot peel or cold peel. The average results with seven samples of the oil were as follows:—Sp.gr. at 20°/20° C., 0·8563; optical rotation, a_D^{20}, +93·28; n_D^{20}, 1·4758; aldehydes (as octyl and decyl aldehyde), 1·67 per cent.

Since the aldehydes consist of a mixture of approximately equal quantities of octyl and decyl aldehydes, the factor 0·070 for 0·5 *N* acid, corresponding with the molecular weight of a mixture containing equal parts by weight of those aldehydes, was used in calculating the results.

Determination of Basic Dyestuffs by Means of Silicotungstic Acid. E. B. Johnson. (*J. Soc. Chem. Ind.*, 1934, 53, 194–195T.)—The method previously described (ANALYST, 1933, 58, 778) for the determination of methylene blue has been extended to other basic dyestuffs, and provides a rapid method for determining the dye base. About 0·1 grm. of the dyestuff is weighed, dissolved in water containing about 12 drops of concentrated hydrochloric acid, the solution is diluted to 200 ml., and a slight excess of a 5 per cent. aqueous solution of silicotungstic acid, acidified with a few drops of concentrated hydrochloric acid, is added. After being heated for 15 minutes on the water-bath, the coagulated precipitate is left to settle; the supernatant liquid is then decanted through a Gooch crucible which contains an asbestos mat and has previously been dried to constant weight at 120° C. The precipitate is washed twice with hot water by decantation, transferred to the crucible, washed free of chlorides, and dried at 120° C., thus giving the weight of dye base in combination with silicotungstic acid. The organic matter is then ignited, and the residue, $SiO_2 12WO_3$ is weighed, the difference being the weight of dye base in the original dyestuff taken. Since silicotungstic acid, when heated between 120° C. and ignition temperature, loses 4·5 per cent., calculated on the ignited weight of the acid, a correction is introduced. The method can be used when the constitution of the dyestuff is unknown or indefinite. If the constitution is known, it is not necessary to dry and weigh the precipitate obtained, once the arithmetical relation between dye base and residue has been established for one sample of the dyestuff, the relation being expressed as a ratio. Hence, weight of residue × ratio = dye base in weight of dyestuff taken. The ratios for some dyestuffs have been worked out; diamant fuchsine, 0·311; Bismarck brown, 0·272; chrysoidine, 0·317; rosaniline hydrochloride, 0·250; methylene blue, 0·171, and malachite green, 0·243. D. G. H.

Inorganic Analysis

Volumetric Determination of Beryllium in Presence of Fluorine. V. M. Zwenigorodskaja and A. A. Gaigerowa. (*Z. anal. Chem.*, 1934, **97**, 327–332.)—Beryllium in neutral solution may be determined volumetrically by titration with alkali against phenolphthalein. The presence of fluoride in the solution causes formation of a more or less stable complex $[BeF_4]''$; this can be decomposed by conversion into calcium fluoride. The liquid (100 ml.) is treated with 2 to 3 drops of one per cent. phenolphthalein solution and 20 ml. of 20 per cent. calcium chloride solution, and titrated with carbonate-free 0·1 *N* sodium hydroxide until an intense pink tint is produced, which does not disappear after 30 seconds' agitation. The solution is then heated to boiling, and titrated to a permanent slight pink. The flask is cooled in running water, which may cause a deepening of the colour; if so, the excess of alkali is determined with 0·1 *N* acid. The determination is repeated, and the mean taken. The procedure is in use as a rapid technical method for the determination of water-soluble beryllium in sintered products and residues. W. R. S.

Separation of Beryllium from Aluminium and Iron by means of Hydroxyquinoline. V. M. Zwenigorodskaja and T. N. Smirnowa. (*Z. anal. Chem.*, 1934, **97**, 323–326.)—In the separation process by hydroxyquinoline in acetate solution (Kolthoff and Sandell, ANALYST, 1928, **53**, 508), oxalic acid interferes by forming an aluminium complex, which results in low aluminium and high beryllium results. Hence the addition of 0·2 grm. of oxalic acid (specified in the earlier directions issued by the Siemens and Halske laboratory, and adopted by Frésenius and Frommes, ANALYST, 1932, 57, 271, line 1) is not only unnecessary but harmful. The authors favour the procedure of Kolthoff and Sandell (*supra*).

W. R. S.

Oxidimetric Determination of Cerium by means of Dichromate and Arsenite. R. Lang. (*Z. anal. Chem.*, 1934, 97, 395–401.)—The oxidation of cerous salt with dichromate is induced by arsenite: $Ce_2O_3 + 2CrO_3 + As_2O_3 = 2CeO_2 + Cr_2O_3 + As_2O_5$, provided metaphosphoric acid is present, as this forms cerous and ceric complexes. The ceric salt is titrated with ferrous sulphate. The cerous solution, which may contain 5 to 30 ml. of hydrochloric, or 3 to 40 ml. of sulphuric, or 5 to 50 ml. of nitric, acid (all strong) in 200 ml., is treated with 4 to 5 grms. of vitreous metaphosphoric acid dissolved in 20 ml. of water, and 0·1 ml. of diphenylamine solution (1 grm. in 100 ml. of syrupy phosphoric acid). The solution is stirred during addition of dichromate (15 grms. per litre) and arsenite (15 grms. As_2O_3 and 10 grms. Na_2CO_3 per litre) solutions. For quantities up to 0·35 grm. Ce, 30 ml. of dichromate, and 35 to 40 ml. of arsenite, solution are recommended. After an interval of half a minute, the deep-blue solution is titrated with 0·1 *N* ferrous sulphate solution to a grass-green tint. A correction of 0·015 ml. is required for the indicator. W. R. S.

Rapid Determination of Tungsten in Low-grade Ores. S. Fernančič. (*Z. anal. Chem.*, 1934, 97, 332–334.)—The fine ore powder (0·1 grm.) is ignited in a platinum crucible, evaporated with hydrofluoric and sulphuric acids, and fused with 1 grm. of sodium carbonate. The fusion is extracted with hot water, the manganate reduced with alcohol, and the filtered liquor evaporated almost to dryness in a small porcelain basin. The residue is taken up with 2 ml. of water, the solution treated with 10 drops of thiocyanate solution, diluted to 5 ml. with water, and to 9·5 ml. with strong hydrochloric acid. Titanous chloride solution (15 per cent.) is added, drop by drop, in slight excess, and the yellow coloration is matched against that produced by a neutral tungstate solution (0·0001 to 0·001 grm. WO_3 per ml.), treated with 1 ml. of 0·5 *N* sodium carbonate, and thiocyanate solution, etc., as in the case of the assay. If the sample contains more than 0·5 per cent. WO_3, the solution to be matched is diluted to 15 or 20 ml. with hydrochloric acid (1:1). With products containing less than 0·02 per cent. WO_3, more than 0·1 grm., as well as more flux, is required. The alkaline filtrate of the soda fusion is treated with a slight excess of acid, and a little ferric chloride solution (0·01 grm. Fe); the hot solution is made barely ammoniacal, the precipitate is collected, ignited and fused with 0·5 grm. of sodium carbonate, and the fused mass is treated as described above. W. R. S.

Separation of Phosphoric Acid, Calcium and Magnesium. H. Brintzinger and E. Jahn. (*Z. anal. Chem.*, 1934, 97, 312–314.)—The procedure is based on the insolubility of calcium molybdate. Phosphoric acid is precipitated as ammonium phosphomolybdate; the filtrate is evaporated to about one-half its bulk, and made ammoniacal. If necessary, more precipitant is added (weakly ammoniacal ammonium molybdate solution); when cold, the solution is treated

with alcohol until cloudy. When the crystalline precipitate has settled it is collected, dried, and ignited to constant weight. If a paper filter is used, the precipitate and paper should be ignited separately. Magnesium in the filtrate from the calcium precipitate is recovered, as usual, in the form of ammonium magnesium phosphate.
W. R. S.

Determination of Inorganic Phosphate in the Presence of Arsenic. L. B. Pett. (*Biochem. J.*, 1933, **27**, 1672–6.)—In the colorimetric determination of phosphorus, the interference due to arsenates may be eliminated by reducing them to arsenites. The method was devised during the study of the effect of arsenates on phosphatase activity, and is claimed to give good results even when the arsenate concentration is *M*/10 in the presence of 0·05 mgrm. of phosphorus. All or part of the trichloroacetic acid filtrate from the enzyme digest is transferred to a 25-ml. flask. Sulphuric acid (0·5 ml. of 3 *N*) is then added, followed by about 0·4 grm. of sodium bisulphite. After a little practice, the necessary amount of bisulphite can be estimated without weighing, and it is introduced into the flask through a funnel. The flask is then placed in a water-bath at 50° C. (±1°) for one hour, after which it is removed, the reagents for determining phosphate added, and the solution diluted to 25 ml. The increased temperature causes a more rapid development of the blue colour than usual, and readings may be made at once with Fiske and Subbarow's method (*J. Biol. Chem.*, 1925, **66**, 375), or in fifteen minutes with Brigg's modification (*J. Biol. Chem.*, 1922, **53**, 13; 1924, **59**, 225; Abst., ANALYST, 1922, **47**, 409) of Bell and Doisy's method (*J. Biol. Chem.*, 1920, **44**, 55). The standards should be developed for at least three minutes at 50° C. in order to ensure a stable colour intensity. S. G. S.

Microchemical

New Micro-method for the Detection of Monoses in the Presence of Reducing Bioses. H. Tauber. (*Mikrochem.*, 1933–4, **14**, 167–169.)—The new reagent is similar to Barfoed's solution, except that the volatile acetic acid is replaced by the non-volatile lactic acid. The cuprous oxide formed in the test through the oxidation of the monoses is treated with a molybdate solution, the blue colour developed being proportional to the amount of monose present. The reagent will keep unaltered, and can be used in quantitative work, for blood analysis and the glucosidase reaction (Tauber and Kleiner, *J. Biol. Chem.*, 1932, **99**, 249) in urine analysis (*id.*, *ibid.*, 1933, **100**, 749; Abst., ANALYST, 1933, **58**, 413). *Reagents.*—(i) *Copper-monose reagent.*—Twenty-four grms. of copper acetate (pure) are dissolved in 450 ml. of boiling water. Any precipitate formed should not be filtered off. To the hot solution, 25 ml. of an 8·5 per cent. solution of lactic acid are added. On shaking and boiling for a short time, the precipitate is mainly dissolved. When cold, the mixture is filtered and diluted to 500 ml. (ii) *Molybdate solution.*—This is the same as described by Benedict (*J. Biol. Chem.*, 1931, **92**, 141).

Method.—One drop (0·05 ml.) of the neutral monose-biose solution is placed in a micro-test tube. This solution should be so diluted that the total reduction is not more than 1·25 mgrm. per ml., or less than 0·05 mgrm. per ml. in glucose equivalents, supposing the solution to contain glucose and lactose. If the solution contains glucose and maltose, the total reduction must not exceed 0·5 mgrm. per ml. Sucrose may be present up to 2·5 mgrms. per ml. without interfering with the test. In a second micro-test tube a drop of water is placed for a blank test. A drop of the copper-monose reagent is added to both tubes, which are then placed for 8 minutes in a boiling water-bath and cooled for 2 minutes, after which a drop of the molybdate solution is added. After 2 minutes' shaking, 10 drops of distilled water are added. A blue colour indicates monoses, and is proportional to the amount present. Chlorides and some other inorganic salts interfere, but as much as 1·5 mgrm. per ml. of sodium chloride may be present without interference. The smallest amount of glucose (or other monose) detectable in this way is 0·0025 mgrm. J. W. M.

Use of Benedict's Solution in the Micro-Detection of Sugar in Urine and other Solutions. H. Tauber. (*Mikrochem.*, 1933–4, **14**, 169–170.)—*Reagents.*—Copper sulphate (crystalline) 17·3 grms., sodium citrate 173·0 grms., sodium carbonate (anhydrous) 100 grms. The sodium citrate and sodium carbonate are dissolved in 750 ml. of water and filtered. The copper sulphate is dissolved in water and poured into the carbonate-citrate solution, and the whole is diluted to 1 litre with water.

Method.—A drop of the clear or filtered urine (or test solution) is mixed with 0·5 ml. of the Benedict's solution in a micro-test tube and heated for 2 minutes over a boiling water-bath. After cooling, if glucose is present, a red, yellow or greenish precipitate appears, the colour depending upon the amount of glucose present. When more than 0·2 per cent. of glucose is present the precipitate is formed rapidly. *Detection limit.*—0·03 mgrm. of glucose in a drop (0·05 ml.). J. W. M.

Determination of Iodine in Organic Compounds. J. L. Goldberg. (*Mikrochem.*, 1933–4, **14**, 161–166.)—Organic iodine is converted into ionic iodine by the usual Pregl method (*Quantitative Organic Microanalysis*, 2nd Ed., 1930, p. 118), but without the use of bisulphite. After the combustion the carbonate solution containing the absorbed iodine is washed into a conical flask, and neutralised (methyl orange) with N sulphuric acid, 0·1 ml. in excess being added. The acidified solution should not exceed 75 ml. One ml. of saturated bromine water is then added, and the solution is shaken and allowed to stand for 2 minutes. Excess of bromine is removed by the addition of 1 ml. of a 5 per cent. solution of phenol (quinone-free). After being shaken and left for 2 to 3 minutes, the mixture is treated with a solution of 1 grm. of potassium iodide (iodate-free) in a few ml. of water, and the liberated iodine is titrated with 0·02 N thiosulphate solution. The procedure gives excellent results provided that: (i) The acidity of the solution to which the bromine is added is low; the excess acid must not be more than 0·2 ml. (ii) The phenol is added in one portion; otherwise tribromophenol or tribromophenol bromide may be formed, which liberates iodine from potassium iodide and yields results too high. One ml. of saturated bromine water provides sufficient bromine to oxidise 4 mgrms. of iodine. Blank determinations gave no starch-iodine colour. The use of phenol for removing the excess of bromine was found superior to Leiperts' method of boiling (*Pregl-Festschrift Mikrochem.*, 1929, 266; Abst., ANALYST, 1930, 55, 413), which may give low results. Salicylic acid and aniline sulphate were also tested, but gave poor results. J. W. M.

Micro-determination of Iron. F. Rappaport and E. Hohenberg. (*Mikrochem.*, 1934, 14, 119–128.)—The method consists in the reduction of ferric iron with iodide, the iodine liberated being determined by titration with *N*/200 thiosulphate solution after oxidation to iodate with bromine. The reduction is carried out in the Parnas and Wagner modification of the micro-Kjeldahl apparatus (Pregl, *Quantitative Organic Microanalysis*, 2nd English Edition, 1930, p. 111). The test solution is placed in the distillation flask, and 2 ml. of 20 per cent. sulphuric acid are added. Steam is passed through the apparatus until all the air has been displaced, after which 2 ml. of a potassium cadmium iodide solution are added. This solution contains 1 grm. of potassium iodide in 20 ml. of a 20 per cent. solution of cadmium sulphate; the cadmium sulphate solution will keep, but the potassium iodide should be added just before use; the heat-resistant $K_2(CdI_4)$, which is formed from the excess of iodide, prevents the liberation of iodine. In the conical receiver flask are placed 2 ml. of a mixture of 20 parts of 0·1 *N* sodium hydroxide solution and 15 parts of 2 per cent. sodium sulphite solution, and the distillation is then carried out. If the test solution contains iron, the contents of the distillation flask first turn yellow, and are then decolorised as the iodine distils over into the receiver. The distillation is continued for 2 minutes with the condenser tube dipping into the receiver solution, and for a further 2 minutes with the receiver lowered. Then 5 drops of methyl red (15 mgrms. in 100 ml. of *N*/100 alkali) are added to the solution in the receiver, followed by 20 per cent. sulphuric acid until the reaction is just acid. Three ml. of 15 per cent. sodium acetate and a few drops of a solution of 3 ml. of bromine in 100 ml. of glacial acetic acid are then added, until the solution remains yellow-brown with bromine. After 2 minutes the excess of bromine is decomposed with formic acid, added drop by drop, any bromine vapour remaining in the flask being drawn off by means of the pump, and 2 ml. of 20 per cent. sulphuric acid are then added. Potassium iodide is introduced, and the liberated iodine is titrated with thiosulphate solution. Good results were obtained with pure ferric salts, even in the presence of a large excess of phosphoric acid. For the determination of iron in the ferrous state the iron is first oxidised to the ferric condition by means of iron-free nitric acid; 2 ml. of the test solution are diluted with 3 ml. of water, 0·5 ml. of nitric acid are added, and the mixture is heated for 5 minutes on the water-bath, to complete the oxidation, after which the oxidising action of the nitric acid is stopped by adding 2 ml. of a 40 per cent. solution of urea, and heating the mixture for a further 2 minutes. The determination is completed as before. Any free hydrochloric acid must be neutralised with sodium hydroxide and the solution then slightly acidified with sulphuric acid before the oxidation of the iron to the ferric state. Iron-containing organic substances are ashed in the wet way in micro-Kjeldahl flasks, sulphuric acid and perhydrol being used, and any excess of perhydrol destroyed with titanium salts, which also catalyse the decomposition of organic matter. The sulphuric acid for ashing contains 33 ml. of sulphuric acid, 2 grms. of ammonium sulphate and

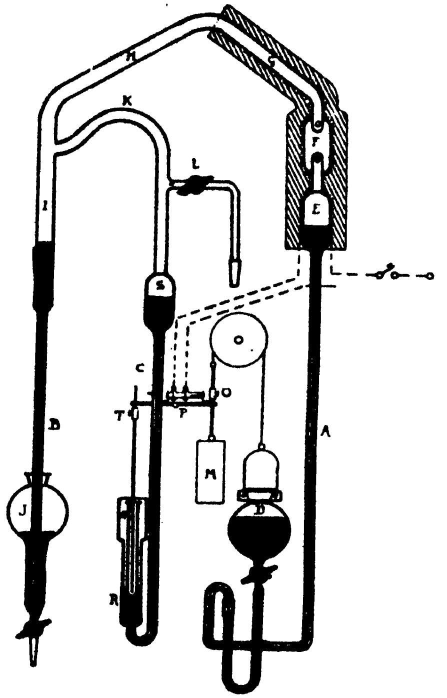
0·45 grm. of titanium hydroxide, and is diluted with water to 100 ml.; 2 ml. of this solution are used together with 0·1 ml. of perhydrol. A further 1 ml. of perhydrol is added later, and the heating is continued until the disappearance of the orange-red colour of the titanium peroxide. The figures given for determination of 0·04 to 1·6 mgrm. of iron show errors varying from 0·5 to 5 per cent. J. W. M.

Micro-determination of Calcium in Serum. P. Wenger, C. Cimerman and P. Bongland. (*Mikrochem.*, 1933–4, **14**, 140–158.)—Various methods are discussed and investigated, and 17 references are given. The method recommended is incinerating the material in a micro-platinum crucible, transferring the contents to a micro-beaker with two drops of concentrated hydrochloric acid and 2 to 3 ml. of water, neutralising the solution to methyl red with ammonia, precipitating with ammonium oxalate over a water-bath, and, after an hour, filtering off in an Emich filter-stick of glass, with an asbestos plug. Instead of weighing the washed precipitate, it is determined by titration with $N/100$ permanganate solution, 0·01 ml. being subtracted from the result as a correction for the permanganate reduced by the asbestos. J. W. M.

New "Spot" Test for Potassium. N. S. Poluektoff. (*Mikrochem.*, 1933–34, **14**, 265–266.)—The test depends on the formation of the sparingly soluble orange-red potassium salt of hexa-nitro-diphenylamine (*p*-dipicrylamine) $(C_6H_2[NO_2]_3)_2NH$. The amine is soluble in ammonia and sodium hydroxide solution, giving an orange-red solution, which turns yellow on acidification, with precipitation of the amine in yellow flecks. The test is carried out on filter-paper (fine thick "spot" paper is best). A drop of the neutral test solution is placed on the paper, followed immediately, before the drop has diffused, by a drop of the reagent solution (0·2 grm. of the amine dissolved by heating to boiling with 2 ml. of N sodium carbonate solution and 20 ml. of water; this is filtered when cold). An orange-red fleck forms at once; one or two drops of 2 N hydrochloric acid are then placed on the fleck, which remains unchanged in the presence of potassium. In the absence of potassium the colour changes completely to sulphur-yellow. This reaction is specific for potassium in the presence of lithium, sodium, magnesium, strontium, calcium, and barium. If ammonium salts are present in excess, they should be removed. Rubidium and caesium react in the same way as potassium, and should be absent. *Limit of identification.*—3·0γ potassium. *Concentration limit.*—1 : 10,000. *Proportion limits.*—K : Li = 1 : 130, K : Na = 1 : 180.
J. W. M.

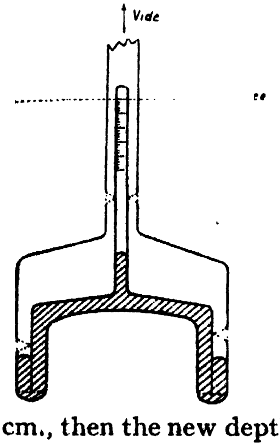
Physical Methods, Apparatus, etc.

Apparatus for the Distillation of Mercury under Reduced Pressure. H. Vogels. (*Bull. Soc. Chim. Belg.*, 1934, **43**, 327–330.)—The apparatus, which is made of Pyrex glass, has three capillary barometric tubes. The first, A, is attached by means of rubber tubing to the reservoir bulb, D containing the impure mercury. At the top of this tube is an expansion, E (25 mm. in diameter), which is electrically heated by means of a coil. The vaporised mercury passes into a second expansion, F, and thence, through the tube G, into H, where it is condensed by air-cooling, the drops falling into I and collecting in the reservoir J, from which the purified mercury can be drawn without interrupting the distillation. The evacuation of the apparatus is effected through the tube K, the pump being controlled by the tap L. To prevent the heating continuing after all the mercury has been drawn from the reservoir D, an automatic device is provided for cutting off the current. The flask D is attached, by means of a cord passing over a pulley, to the counter-weight M, the weight of which is equal to that of D when nearly evacuated. When the weight of D becomes less than that of M, a catch, O, on the rod of the counter-poise, descends and acts on the lever P, which carries a small mercury contact; the circuit is thus broken.



The column C is intended to protect the apparatus from the consequences of the accidental admission of air. A float, Q, rests on the mercury in the tube R. As the pressure increases in the upper part of the apparatus the float Q begins to rise, and the catch T on the rod that is carried by the float acts upon the lever P, which controls the current. The object of the bulb S is to increase the sensitiveness of the safety device.

By raising the bulb D it is possible to make the apparatus work at any desired reduction of pressure, and thus avoid the drawback that at very reduced pressures some of the noble metals may distil with the mercury. Before distillation the mercury must be freed from the usual metallic impurities by prolonged washing with mercurous nitrate solution or with ferric sulphate solution.



Direct Reading Manometer for Low Pressures. F. Trombe. (*Bull. Soc. Chim.*, 1934, [5], 1, 408–410.)—The McLeod gauge is inconvenient for the measurement of low pressures, particularly as it is suitable only for perfect gases containing no vapours liquefiable at the temperature of measurement. If, however, a thin glass bell-jar of uniform thickness is filled with mercury and inverted on a mercury surface, it will assume a position such that when a vacuum is applied over the surface, its weight will be in equilibrium with the pressure of the mercury on the walls. If a small amount of air is then allowed to enter the space over the supporting mercury surface, so as to produce a pressure of p grms. per square cm., then the new depth of immersion will be $pD_1^2/d(D_1^2-D_2^2)$, where D_1 and D_2 are the exterior and interior diameters of the bell-jar, respectively, and d is the density of mercury; with a bell-jar 7 cm. in diameter and 1 mm. thick, changes in height corresponding with variations in pressure of 1 to 0·002 mm. may be measured micrometrically. The figure shows a section of the apparatus; the outer vessel is shaped as shown in order to economise mercury, and the bell-jar, which is held in a central upright position by the small spurs, is extended into an upper central tube carrying the graduations. The weight of air displaced by the emergent portion of the bell-jar is ordinarily negligible. The apparatus may be used in conjunction with electrical methods of control, and, if a thinner or wider bell-jar is used, pressures of 0·001 mm. may be measured. J. G.

Fluorescence Test for Olive Oils. T. T. Cocking and S. K. Crews. (*Pharm. J.*, 1934, **133**, 86).—With filtered ultra-violet radiations virgin olive oils usually give a golden-yellow fluorescence, whereas refined and adulterated oils give a bluish fluorescence. Treatment of the oil with decolorising charcoal is a useful adjunct to this test. To about 100 ml. of the oil 5 grms. of decolorising charcoal are added, in portions of about 1 grm. at a time, over a period of six to eight hours, the mixture being frequently shaken during that time. After the mixture has stood overnight, the supernatant oil, which should be almost colourless, is poured off and filtered. The fluorescence is then noted through Chance's "Ultra-violet" glass. Oils giving a low Bolton-Williams number also give a distinct blue fluorescence. A table showing the colour obtained with a large number of treated and untreated oils is included. S. G. S.

Fluorescence and Detection of Rhapontic Rhubarb. T. E. Wallis and E. R. Withell. (*Pharm. J.*, 1934, **133**, 90.)—Ten per cent. of rhapontic rhubarb may be detected in Chinese rhubarb by direct examination of the powder under ultra-violet light, genuine Chinese rhubarb being used as a standard. The genuine rhubarb gives a velvety brown fluorescence, whilst an adulterated sample exhibits a purple fluorescence. Five per cent. of adulteration may be detected by the above procedure, with the use of a hand lens to examine the powder, when the presence of rhapontic rhubarb is denoted by shining violet points. Less than 5 per cent. may be detected by the following process:—The sample under examination and a sample of genuine Chinese rhubarb are separately macerated in alcohol in the dark (one part of the drug in 50 volumes of 95 per cent. alcohol). The tinctures are filtered, and strips of wood cellulose absorbent paper are immersed in the filtrate, removed and dried in the dark. They are then examined under ultra-violet light. Rhapontic rhubarb is indicated by a violet fluorescence in the strip under examination, the strip from the macerate of Chinese rhubarb being used for comparison. As little as 1 per cent. of Austrian rhapontic rhubarb can be detected by this method. S. G. S.

Reviews

RICHTER'S ORGANIC CHEMISTRY. Vol. I. CHEMISTRY OF THE ALIPHATIC SERIES. Newly translated and revised from the 12th German Edition by E. N. ALLOTT. Pp. xiv + 790. London: Kegan Paul & Co. 1934. Price 35s.

The present (6th English) edition follows closely the lines of its predecessors, but much of the subject-matter has been revised up to 1932.

Richter's Chemistry is an apotheosis of organic compounds as such: Opening the book at p. 200 we find descriptions of some seventeen compounds, and this intensity is well maintained with eighteen descriptions on p. 400 and fifteen on p. 600. Section headings such as "Hydroxamic Oximes," "Alkyl Derivatives of Beryllium," "Mercaptals," "Amino-Ketones," and "Diolefine Dicarboxylic Acids," guarantee that no normal type of compound is omitted.

This book will remain a standard work of reference to the many who find the price of the 4th edition of "Beilstein" prohibitive, and consequently it is gratifying to find that the revision has been extensive. To single out one or two points: concise accounts are given of the electronic theory of valency (3½ p.) and of the parachor (1 p.); the analytical section now contains a description of micro-methods; Ruzicka's work on the dicarboxylic acids is outlined; the section on the sugars has been rewritten; and reference is made to recent work on spermine, the porphyrins, the sulphoxides, asymmetric tellurium compounds, the structure of *iso*-cyanides, aliphatic diazo-compounds and nitroparaffins.

It is a pity that the old formulae for the sterols and the bile acids have crept through without comment, and it is rather odd to have "Centralblatt" references to Kipping's work on asymmetric silicon compounds, and to that of Pope and Peachey on asymmetric tin compounds. In this connection it should be mentioned that most of the "Centralblatt" references from 1910 onwards have been replaced by their original sources.

Manufacturing processes are less adequately dealt with, and there appears to be a singular reluctance to mention the uses and applications of many substances. Thus dihydroxymaleic acid and thiocarbamide appear without comment; the modern catalytic method of preparing maleic anhydride is not mentioned, and there is no reference to the important applications of this compound devised by Diels and Alder.

Here and there a few loose statements are to be found, such as "The *chief use* of potassium cyanide is in the preparation of acid nitriles." Sometimes an unimportant derivative is mentioned and an important one omitted; for example, although $CO(NH_2)_2.NaCl.H_2O$ is described, no reference is made to hyperol. The excellent method of preparing ketones and aldehydes by passing carboxylic acids over heated thoria or titania is not given, nor is there any reference to Sasaki's elegant synthesis of α-amino-acids. Finally, it is rather late in the day to quote Landolt's *Optische Drehungsvermögen* of 1898 for the literature of the resolution of racemic compounds.

These minor criticisms are put forward as suggestions for future consideration, and not to minimise the sterling merit of the book under review. J. KENYON.

SOIL ANALYSIS. By C. HAROLD WRIGHT, M.A., F.I.C. Pp. viii+236. London: Thos. Murby & Co. Price 12s. 6d. net.

The author has recorded in this book a very considerable amount of information concerning soil analysis, much of which so far has been published only in journals and similar publications.

The early chapters include methods for the determination of the heat of wetting, soil shrinkage, moisture-content at the point of stickiness, density and pore-space, etc. These methods, though perhaps only occasionally required in the majority of laboratories, are carefully described so that they may be followed by anyone with laboratory experience, the details of the processes being apparently complete.

Possibly one of the most important portions of the book is that devoted to the mechanical analysis of soil, and here several processes are recorded, the author, perhaps wisely, refraining from recommending any one procedure. The process recently published by the Imperial Bureau of Soil Science is given at length, but no suggestion is made that analysts should in the future use the process and thereby adopt a uniform procedure. Possibly the author, even with his large experience, has not had occasion to use the several processes described on the same soil, and therefore could not record information about the probable differences to be obtained by the use of them. The soil analyst is left to choose his own process, and to assume that all the processes give similar results.

Methods for the determination of nitrogen, ammonia, nitrates and nitrites do not occupy a dozen pages, but those that have been well tried are invariably given.

The study of base exchange, including the determination of individual exchangeable bases, rightly occupies considerable space, and this is in accordance with the importance of the subject at the moment.

Often information on a subject is somewhat "spread out," with the consequence that references are made several times on many pages to other pages of the book. The turning-over of pages to follow a subject through is, at least, a little disturbing, but is unavoidable with the author's method of compilation. As an example, Woy's method for the determination of phosphoric acid is criticised on one page and described many pages further on, and the necessary factors are given in still another part of the book.

Some twelve pages of the book are devoted to the preparation of standard solutions for volumetric analysis, and it is a matter of opinion how great a want these supply. Probably most of this information could be entirely dispensed with, for it is of little use to the practising analyst, and surely a student should be taught to look for knowledge of this type in books specifically dealing with the subject.

To the soil analyst the book is a most serviceable and useful volume, and to the student it is indispensable as a work of reference, for between its covers a large amount of information on soil analysis has been collected from very scattered sources.

F. W. F. ARNAUD

THE LABORATORY: ITS PLACE IN THE MODERN WORLD. By D. STARK MURRAY, B.Sc., M.B., Ch.B. Pp. 117. London: The Fenland Press. 1934. Price, paper 2s., cloth 3s.

This little book is intended for the lay reader, and not for the scientist, to whom the use of a laboratory is familiar. The large number of industries which need research or routine laboratories are mentioned, and also the very varied range of subjects on which laboratory work is carried out. Several chapters are devoted to medical laboratories and their work, of which the pathological side is emphasised. No figures or statistics are given of the numbers of qualified and unqualified workers in the different branches of scientific work, or of costs of laboratories and salaries of the workers. There is no index, but it is, perhaps, unnecessary in such a slight summary of the subject.

JANET W. MATTHEWS

AN ENQUIRY INTO THE NATURE OF CERTAIN NINETEENTH-CENTURY PAMPHLETS. By J. CARTER and G. POLLARD. Pp. xii+400. London: Constable & Co., Ltd. 1934. Price 15s. net.

In a way this book symbolises a court of justice in which the authors, acting as counsel for the prosecution, formulate a charge of wholesale forgery against some person or persons unknown, produce expert evidence in support of the charge, and ask the jury, their readers, to find a verdict of guilty.

The authors' case is that a large number of treasured "first editions" of pamphlets by leading Victorian writers cannot be accepted as genuine. These impugned publications, which include works by such authors as Browning, Mrs. Browning, Tennyson, Thackeray, William Morris, and Ruskin, have been acquired, sometimes at high prices, by the British Museum and other public libraries, and by private collectors, and some of them even contain autographed signatures of their authors, admittedly inscribed at much later periods than the reputed dates of publication. There appears to have been a constant supply of these rarities, although it was well regulated to prevent flooding of the market, and this had led to vague suspicions and uneasy rumours, in which suggestions of forgery were implied. With the hope of bringing some degree of certitude into such an unsatisfactory position, the authors decided to subject these questionable pamphlets to critical examination, and in the first part of their book they present the evidence they have secured.

This evidence begins with a critical summary of the various accounts of how Mrs. Browning's *Sonnets from the Portuguese* was first given to the world, and it is shown that the traditional story, that the manuscript was sent to Miss Mitford in 1847, to be secretly printed at Reading, involves so many inconsistencies as to raise a strong presumption that the alleged first edition of that work is spurious.

In Chapter IV the chemical evidence is produced. It opens with a well-written summary of the history of paper-making materials, and then discusses the established data in relation to the books under suspicion. Since esparto was not in use until 1861 and chemical wood pulp not until 1874, any paper containing those materials must have been made at respectively later dates. The presence of esparto in ten of the pamphlets prior to 1858 is therefore inconsistent with their being genuine, and the same conclusion applies to thirteen of the other pamphlets, which contain a significant amount of chemical wood and yet bear dates from 1842 to 1873.

This chapter shows plainly the hand of the chemist. In their preface the authors acknowledge their indebtedness to Messrs. Cross & Bevan, to Dr. C. J. Fox, and to Mr. A. G. S. Hebbs, but in the chapter itself there is no mention of any analysts other than the authors themselves, where they say (p. 54): "Our third group consists of those pamphlets in which we found an unmistakably significant proportion of chemical wood." One cannot help having a shrewd suspicion that in this and several other passages counsel have identified themselves rather too closely with their witnesses, and that there should have been a number of inverted commas throughout the chapter.

Equally telling is the evidence provided by an examination of the type of the pamphlets. In 1883 the firm of Clay & Taylor introduced into their founts new forms of "f" and "j," in which the usual kern (*i.e.* the curl projecting beyond the face of the type) was lacking. Now, sixteen of the pamphlets (including Mrs. Browning's *Sonnets*), dating from 1842 to 1873, have these kernless "f's" and "j's," and are admitted by Messrs. Clay to have been printed by them. Unfortunately, they have preserved no ledgers earlier than 1911, and are, therefore, not in a position to say for whom the printing was done.

Additional evidence of a similar kind is afforded by the defective character of the blocks in these reputed "first editions," when compared with those in authenticated editions of later date; the inference is that the former were copied from the latter.

This part of the book concludes with a summary of the proved conclusions, and no one who has studied the evidence can fail to come to the decision that the authors have established their case.

In Part II an attempt is made to reconstruct the circumstances in which the forgeries were conceived, and the methods by which they were carried out and put into circulation. Here the deductions are more conjectural than those drawn in the first part, since they are more dependent on human testimony and less on circumstantial evidence. Part III contains the dossiers of each of the pamphlets examined, and the work concludes with an excellent index.

Regarded as a whole, this book must be accepted as a notable contribution to bibliography; scientifically, it is important, as the outcome of work in which, probably for the first time, the chemist has been called upon to aid in the solution of a literary problem.

EDITOR

OCTOBER, 1934 Vol. 59, No. 708

THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

Deaths

WITH great regret we record the death of

VISCOUNT DEVONPORT,

who was made an Honorary Member in recognition of his Parliamentary services to the Society; also of

ALFRED WALTER STOKES,

who was one of the earliest Members of the Society, and contributed numerous papers to THE ANALYST in 1881 and the following years, but had left the Society some years before his death.

Old Masters and Modern Forgeries

BY A. P. LAURIE, M.A., D.Sc., F.R.S.E.

(*Professor of Chemistry to the Royal Academy of Arts*)

(*Lecture delivered at the Summer Meeting, North of England Section, June 22nd,* 1934)

IN my former lecture to this Society (*cf.* ANALYST, 1930, **55**, 162) I dealt mainly with the chemical methods of examining the pigments of paintings; to-day I propose to give a more detailed account of the use of other scientific methods that enable one to form a judgment as to the authenticity of a picture. It will be remembered that the chemical examination consists in removing a minute fragment from the surface of the picture by means of a micro-borer made from a hypodermic needle, and subjecting the particle to a series of microchemical tests in order to identify the pigment or pigments of which it consists.

Systematic examination of a very large number of paintings has established the fact that certain pigments were in use at one time, but not at another, and that it is therefore often possible to determine within relatively narrow limits the period within which a picture must have been painted. For example, a very beautiful azurite, owing doubtless to the discovery of a fine deposit, became a fashionable pigment about 1450, even replacing ultramarine, and disappeared altogether from the artist's palette about 1650. Smalt, again, was not used before the latter part of the sixteenth century, and Prussian blue does not appear in the artist's palette until the middle of the eighteenth century. The classified results of these chemical tests have been tabulated in a chart (ANALYST, 1930, **55**, 176), which shows at a glance the pigments in use at successive periods, and thus may help to date a particular painting.

This microchemical method has also given us a knowledge of the pigments used by the great masters, and this may be a decisive factor in determining whether a doubtful picture has been correctly attributed to a particular artist.

An interesting trial, in which the chemical evidence was an important factor, was the libel action brought against Lord Duveen for saying that Mr. Hahn's version of the picture "La Belle Feronnière" was a copy of the picture in the Louvre attributed to Leonardo da Vinci. There were two versions of this picture in the possession of Louis XIV—one the original and the other a copy. Mr. Hahn claimed that his version was the original. The microscopical examination of the two pictures was most informing. Leonardo da Vinci has left an account of the pigments he used for painting flesh; these I found in the Louvre picture, whereas the pigments in the Hahn picture, although also old, were quite different.

The owners of "Old Masters" upon which doubt has been thrown are sometimes unduly perturbed by the idea that a chemical examination, the result of which will be invisible to them, will damage the picture, while they accept without demur the injury which may have been done to the painting by destructive restoration; for the early nineteenth-century restorers were seldom content with restoring flaws in the surface and could not resist the temptation of retouching the painter's work.

Notwithstanding these considerations, many owners still have a concealed preference for optical methods of examination, and, fortunately, these are frequently very effective.

PRELIMINARY EXAMINATION.—When a picture is submitted for scientific examination one of the first steps is to make exact measurements of the size of the panel or canvas. It was a common practice of the art patrons of the seventeenth and early part of the eighteenth century to keep a favourite painting at their principal residence and to have replicas of it made to hang at their other seats, but no care was taken to see that these copies were made to the precise dimensions of the original. Not infrequently a descendant of the first owner of a picture has sold the original and contented himself with the copy, and this, in time, may have come to be accepted as the original.

The dimensions of most of the authenticated works of the old masters have been recorded, and a copy of one of them claiming to be the original may thus be eliminated at once by not corresponding with the measurements of the record.

A general survey of the picture is then made under a low magnification of about two to three diameters, and for this purpose the Zeiss magnifier is particularly useful. This is a binocular magnifier provided with an adjustable band which can be passed round the back of the head to keep the glass steady while leaving the hands free to move the picture into different positions.

Among the points to which attention is directed in this survey are the signature or any other distinguishing mark that may be present, the condition of the canvas, indications of restoration and retouching, the condition of the varnish, etc.

The Travelling Microscope.—Owing to the large area that has to be traversed when examining an oil painting it is essential to have a rigid microscope stand, which can be used with a binocular magnifier, a Greenough binocular body, or with the "Ultropak illuminator." The construction of the stand for the examination of hanging pictures differs from that required for examining horizontal pictures on a table; both forms have been designed by Messrs. Leitz (London), Ltd.

The arrangement for suspended pictures is fixed on two wall brackets supporting a rail, upon which moves on rollers a carriage holding the microscope placed horizontally. This microscope has the usual coarse and fine adjustments, but is also provided with a traversing arrangement working on ball-bearings, which allows of a displacement of 2 inches in either direction; the height is adjusted by raising or lowering the picture, which hangs on pulleys between the two brackets.

For inspection of horizontal pictures not exceeding 48 inches in width, the microscope is mounted on a rail similar to that used with vertical pictures and moves on rollers, and the fine adjustment is made by means of a travelling device on ball-bearings. For the coarse adjustment in either direction the rail rests at both ends on a carriage, also moved on rollers on rails, between which the picture lies. The microscope tube is provided with an inclined eyepiece to facilitate observation.

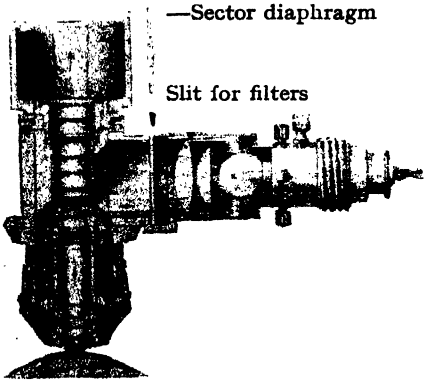


Fig. 1
Ultropak with illuminating apparatus screwed on

Microscope Illumination.—In a microscopical examination of the surface of a picture the use of a vertical source of illumination has the drawback that light reflected at the lens surfaces of the objective produces a glare that tends to render the image indistinct. This haze is largely eliminated by the use of a method in which the illuminating rays lie entirely outside the path of the rays of the microscope. The "Ultropak illuminator" (Leitz), which is constructed on this principle, is a device which has a side-tubulure and is screwed on to the body of the microscope above the objective. The source of light is a small 8-volt filament lamp which is fitted into a special centring mount, and the lateral rays from which are reflected downwards by an annular mirror fixed at an angle of 45° (see Fig. 1).

Each objective has a special ring condenser which can be rotated so as to obtain a uniformly bright image. This instrument reduces, but does not entirely prevent, the glare from the irregular, varnished surface of a picture, but by the addition of a polarising device the image appears quite sharp, even under a high magnification. In the "Polarising Ultropak" (Fig. 2) the polariser is fitted into the lateral illuminating tube and can be rotated, whilst the analyser is placed just above the objective, where it is attached to the microscope between crossed nicols. When the planes of polarisation of the two prisms are at right angles, all glare from the surface of the object under examination is entirely eliminated.

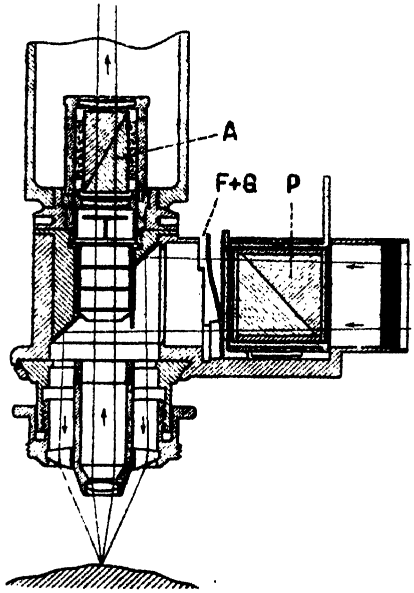
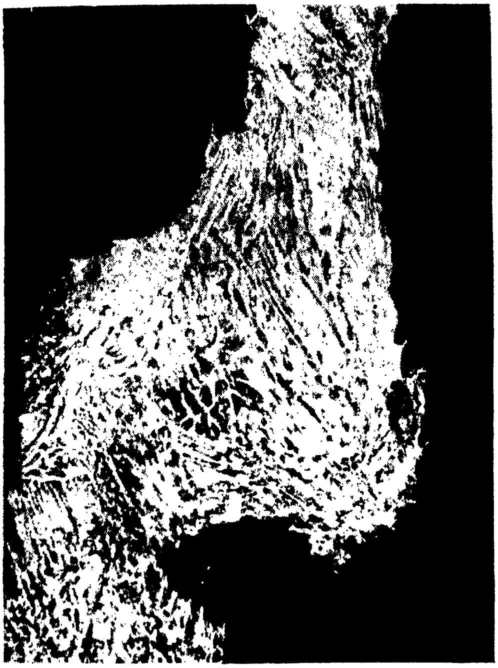


Fig. 2

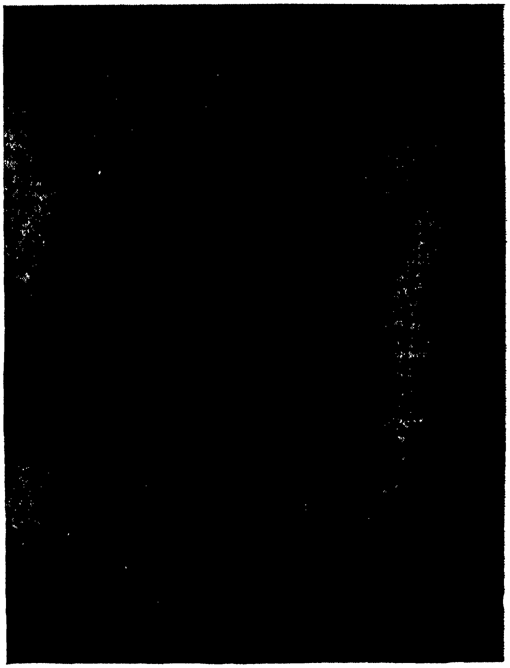
Section of Ultropak with device for use with polarised light (about half-natural size). A, analyser; P, polariser; F + G, slot for filters and selenite plate

In front of the lamp is a recess, with cover, intended for light-filters; these usually include a daylight filter (blue), a heat-absorbing filter (pale green) and yellow-green photographic filters, which may be used separately or in combination.

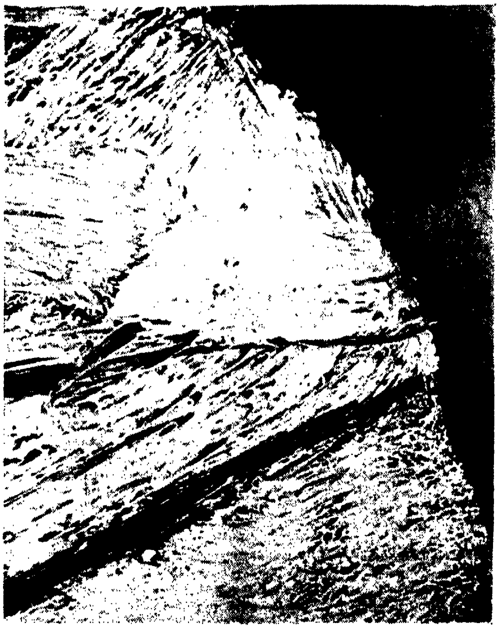
The Painter's Brushwork.—Each of the great masters had a style of applying the paint as distinctive as the writing of his signature, and his characteristic brushwork will be found to run throughout his work, especially that of a particular period. The direct brushwork of Romney (Plate, II), for instance, is very different from the characteristic strokes of Rembrandt, typical examples of which are shown in the Plate (I and III). The peculiar texture of this brushwork suggests that Rembrandt probably used "stand" oil as his medium. This oil has



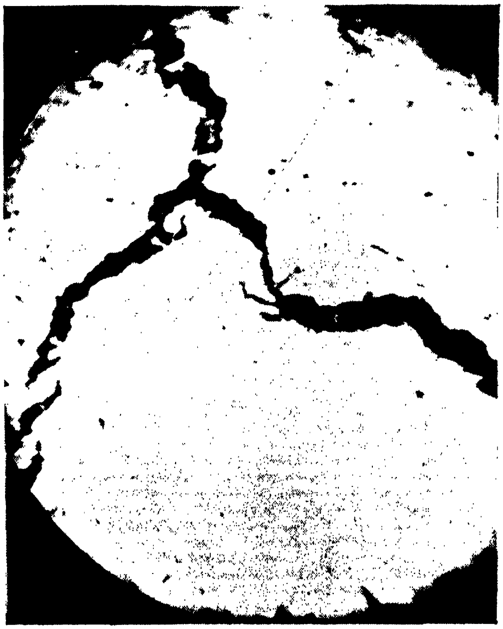
I



II



III



IV

I. Magnified photograph of the nose in the "Portrait of Titus" by Rembrandt (Wallace Collection, No. 29) × 2.
II. Magnified photograph of part of the face in "The Lady and Child" by Romney (National Gallery, No. 1667) × 2.
III. Brushwork of Rembrandt in the "Woman Bathing." (National Gallery, No. 54) × 2.
IV. Cracks in the varnish on an old painting × 40.

been prepared for centuries in Holland from linseed oil, and I have brought together a good deal of evidence indicating that it may have been the kind of oil used by the early Flemish and Dutch painters.

Bol (1616–1680) and other Dutch painters under Rembrandt's influence produced a similar surface, but when magnified photographs are compared, the brushwork is seen to be weak and meaningless compared with that of the master. Further application of this method of examination will probably dispose of the claims of many pictures that have long been accepted as "Rembrandts."

An interesting point in connection with Romney's brushwork is that he sometimes painted on a twilled canvas with hardly any priming, and indications of this surface appear in the finished work.

My idea of studying the brushwork technique of the great painters by means of photomicrographs has frequently proved of the greatest value in deciding who painted a particular picture. One of the earliest instances in which the method was employed was during the Dutch Exhibition, when a press attack was being made on the magnificent Rembrandts in the possession of the Duke of Westminster; it was alleged that these were eighteenth-century forgeries, this judgment being based on a mistaken diagnosis of the wood used in the panels. Photomicrographs of the brushwork, however, showed unmistakably the characteristic strokes of that master.

An important trial in which photomicrographs of the painter's brushwork were material in deciding the issue was the famous Romney case. A picture had been sold in all good faith to an American collector as a painting by Romney of Mrs. Siddons and Miss Fanny Kemble, but was later condemned by one of the leading art experts, and an action was brought by the purchaser to recover the price he had paid. There was no doubt that the picture belonged to the period, and the question at issue was—who painted it? A comparison of photomicrographs of this painting with those of pictures by Romney of about the same date proved beyond doubt that it was not the work of Romney, for, instead of his clear, decisive masterly strokes (*cf.* Plate, II), it showed the uncertain brushwork of a less competent artist. Other evidence supporting this conclusion was obtained by a study of the representation of the facial shadows and of the folds of the drapery in the picture.

The solution of the problem was found by a search of the catalogues of the Royal Academy, which showed that a picture of the two Miss Waldegraves, agreeing with the disputed picture, had been painted by Ozias Humphrey for Horace Walpole. This picture had not met with the approval of Walpole and had been left on the artist's hands. On his death it passed to his son, and its later history could be traced until 1850, when it disappeared. Twenty years afterwards the picture appeared in a private collection as "Mrs. Siddons and Miss Fanny Kemble by Reynolds," in an eighteenth-century frame with a gold plaque, once inscribed with the name of Romney. Ozias Humphrey, who was well known as a miniature painter, took up portrait painting when his eyesight began to fail. He was a friend of Romney, and adopted his style of painting.

Even the artist's brushwork is no longer proof against the ingenious devices of the modern forger. Copies of actual pictures are not made, but pictures are built up by photographing parts of a number of genuine paintings—a bit from one and a bit from another—of, say, Rembrandt, reproducing these on sensitised gelatin, and impressing the gelatin stamp on the prepared soft paint surface. Exact facsimiles of the original brushwork are thus actually present on the panel; the forger paints round these, covers the whole with an "antique" varnish suitably cracked, and finally scrapes off and "restores" the picture in certain places.

CRACKS IN OIL PAINTINGS.—The cracks which frequently cover the whole surface of old paintings are often due to the shrinkage of the layer of paint above the priming, which produces cracks with straight sides. The character of these cracks is clearly shown in a photomicrograph (*cf.* Plate, IV). It is very difficult for a forger to produce cracks that will stand examination under the microscope, although the "cracks" of an old picture on a panel can be imitated so skilfully as to escape detection under an ordinary magnifying glass.

The cracks that occur in mastic varnish are quite different in character from those occurring in oil-paint. They are due to movement in the oil film and show desiccation of the various pigments incorporated therein. Mastic cracks tend to have a web-like form and do not show the long, straight-sided fissures of the paint cracks.

The surface of old pictures varies greatly according to the practice of the painter. Sir Joshua Reynolds was constantly making experiments with mixtures of waxes and balsams, with the result that many of his pictures are in very bad condition, full of cracks. Romney, on the other hand, usually employed only a limited number of pigments ground up with oil, and most of his pictures are in far better condition than those of Reynolds. Very exceptionally, Romney added a little asphaltum to his paint, and the paintings for which it was used are all in bad condition.

The low tone of some of Rembrandt's paintings is due to the surface-varnish having turned yellow; the paint beneath the varnish shows no material signs of deterioration.

REFRACTIVE INDEX.—The refractive index of a minute particle of dried oil is determined by the Becke method, as described by Chamot and Mason (*Handbook of Chemical Microscopy*, Vol. I, p. 369). In this method the fragment is immersed in a liquid of known refractive index, and the movement of the bright peripheral line (known as the Becke line) is observed when the objective is slightly raised from the position of sharp focus. This line appears to move into the medium of higher refractive index, whether this is the particle or the surrounding liquid. By substituting liquids of different refractive index one will be found which yields no Becke line when the objective is raised, thus indicating that this value for the particle and the liquid are identical. The refractive index of the standard liquid is then checked with an Abbe refractometer, as usual. In this way it is possible to determine, with an accuracy of about 0·002, the refractive index of the dried oil particle. Since the refractive index of liquids changes slightly with variation in temperature it is advisable to use the standard temperature at which the liquids have been calibrated for the determination; the temperature of 20° C. is usually adopted.

Fresh linseed oil, as is well known, has a refractive index of about 1·480. This has been found to rise slowly with age, and it seems probable that a refractive index of about 1·600 represents an age of about 600 years—an estimate which is borne out by the examination of known pictures of the thirteenth and other centuries and determination of the refractive index of the oil thereon. Obviously, the method requires prolonged investigation, but it seems to promise valuable confirmatory evidence in assessing the age of a picture. The solvent or liquid applied for the determination of the refractive index does not appear to influence the result, but here again, further work which is required is in progress, as also are tests on the refractive index of egg and other substances that were used as mediums in painting.

An interesting technical question associated with this rise in the refractive index of the oil in oil paintings is the effect of this change upon the translucency of the pigments. Thus a transparent blue, if applied in a thick layer, eventually turns black, and a thin layer of white lead painted over black, gradually becomes transparent and allows the black to become visible again. Whilst this may be due, in part, to slow inter-penetration of the pigment by the oil, with the formation of more transparent soaps, there is no doubt that the increase with time in the refractive index of the oil increases the transparency of the pigment. It has been proved experimentally that pigments which become degraded in tone through a rise in the refractive index of the oil retain their brilliance if painted on a bright under-surface.

The Flemish painter, Van Eyck, and his followers must have understood the optical properties of their pigments and mediums.

X-RAY EXAMINATION.—The value of X-ray photography in the examination of old paintings is that it brings out the structure of the picture, showing the graining of panels, joints glued to the back, nails in the wood, and the difference between the priming and the surface painting. In my former lecture (*loc. cit.*, p. 179) I described the method of taking X-ray photographs, and cited several instances in which the method had shown that certain pictures had been retouched at later periods. One of the most striking of these was the discovery of Dr. de Wild, who found that the Frans Hals picture, "The Toper," in the National Gallery of Scotland, had been retouched at a date later than the original painting. In this case the exact details of the original work indicated by the X-ray photograph were supplied by the discovery of an etching by J. van de Velde (about 1568–1623); this is a portrait of Verdonck, who was a friend of Frans Hals, and it was believed to have been made from a missing painting by Frans Hals. The X-rays thus proved "The Toper" to be the original "Portrait of Verdonck."

An ingenious device of a forger was detected when a suspected "Frans Hals" was subjected to scientific examination. The forger had used an old panel strengthened by battens which had been nailed on from the front, and since the X-rays revealed that modern wire nails had been used, and that the heads of these were below the paint, the picture was a self-evident forgery. This was confirmed by the chemical examination, which showed that the pigments were modern. The painter of the picture was afterwards discovered, and is supposed to have painted his own portrait and to have added the pointed beard and rakish hat required to produce a Frans Hals "gentleman."

THE USE OF ULTRA-VIOLET LIGHT.—Most of the dark inorganic pigments do not fluoresce, and thus dark brown appears black in ultra-violet light. On the other hand, the addition of organic lakes to red lead or to vermilion may often be detected by their distinctive fluorescences. White pigments may also be differentiated; thus, white lead that has been exposed to the air gives a pinkish-brown; zinc white, a yellow or yellowish-green; and titanium white, a deep violet-blue fluorescence. Results obtained with mixtures are more uncertain than those given by the pure pigments alone, and the shade of the fluorescence may be materially affected by the presence of traces of impurities. The fluorescence of the surface varnish or the medium with which the paints were originally mixed may also mask the fluorescence of the pigments.

For these reasons the examination of pictures in ultra-violet light is of value only in exceptional cases, as, for example, when it reveals the fact that parts of the surface have been retouched at a later period or with different pigments. A good example of this was its use in the examination of certain pictures in the Louvre, the authenticity of which had been questioned. The over-painting and retouching revealed by the application of the ultra-violet rays were obvious, and proved that these pictures were not genuine.

Ultra-violet light has also been of service in deciphering the artist's signature on a picture, as is exemplified by a case in which it proved that a doubtful signature of Rubens was really his.

Hence the method should always form part of the routine examination of a picture. The instrument I use is a portable quartz mercury-vapour lamp, the rays from which are projected horizontally on to the picture, which is fixed in a vertical position.

INFRA-RED PHOTOGRAPHY.—Although paint pigments show considerable differences in their absorption of infra-red rays, the method has not proved of much value for distinguishing between them in a painting. On the other hand, the penetrative power of the rays was effective in revealing the details of a signature of Rembrandt of an earlier period, and thus in helping to establish the approximate date of a picture.

In this outline of the application of scientific methods to the examination of the "Old Masters" I have dealt with only some of the lines of investigation still in progress, for the subject is a wide and ever-growing one. To-day there are journals in Germany and the United States of America devoted to the scientific study of the various problems connected with pictures, old and modern. Harvard has a special laboratory devoted to the subject, and the Louvre has also a magnificent one, while in this country the Courtauld Institute is engaged in fitting up a laboratory, and a brilliant young physicist has been added to the staff of the National Gallery.

The Composition and Freezing-Point of Cows' Colostrum

BY G. D. ELSDON, B.Sc., F.I.C.

(*Read at the Meeting of the North of England Section, April* 14, 1934)

IT is a well-known fact that the composition of cows' colostrum (indeed, the colostrum of all mammals, *i.e.* the fluid secreted by the mammary gland immediately prior to and following parturition) differs in a remarkable manner from that of milk as it is ordinarily known.

Results due to Houdet, Vandin, Steinegge, Engling, Kuhn, Richmond, and Carter Bell have shown that colostrum contains less sugar, a fat containing less volatile acids than normal butter-fat, and a very large amount of nitrogenous compounds.

The average of twenty-two analyses of colostrum from different cows by Engling showed: total solids, 28·3; fat, 3·4; casein, 4·8; albumin (and globulin?), 15·9; sugar, 2·5; and ash, 1·8 per cent.

Burr, Berberich and Berg (*Chem.-Ztg.*, 1913, **37**, 69, 97; Abst., ANALYST, 1913, **38**, 107) record the results from twenty different cows giving total solids, 11·8 to 31·1; fat, 1·3 to 9·0; and proteins, 5·1 to 19·3 per cent. The Reichert-Meissl value of the fat varied from 11·5 to 29·1. Similar results have been given by Walker in *Offerton Bulletin*, No. 3.

Crowther and Raistrick (*Biochem. J.*, 1916, **10**, 434; Abst., ANALYST, 1917, **42**, 17) and Woodman (*Biochem. J.*, 1921, **15**, 187; Abst., ANALYST, 1921, **46**, 504) have shown that in colostrum, caseinogen, lactoglobulin and lactalbumin are sharply differentiated and distinct proteins, and that they have the same composition, whether prepared from colostrum or from normal milk. The large increase in total proteins is due, for the most part, to the increase in the amount of globulin present, although the amount of caseinogen is also increased.

Through the kindness of Mr. John Billington, of Irby, we were able to obtain nine consecutive samples of colostrum from each of two cows. These samples were milked at the times stated, placed in a refrigerator at 7 p.m. the same evening, being delivered to the County Laboratory at 9 o'clock the following morning for analysis. For particulars of the two cows and the results obtained see the table on page 666. The cows were milked three times a day: morning 7 a.m., midday 2 p.m., and evening 5.30 p.m.

Cow No. 2 was too weak to be milked on the first day, as it was in a very low condition immediately after calving. Cow No. 1 had a healthy, normal calving, and in this the fat jumped up within the first twenty-four hours and gradually receded to normal, whereas in the case of the very weak cow, the fat-content was very low on the second day, but rose until it was at a maximum on the third day.

Mr. Billington informs us that freshly-calved cows are never milked out for the first two or three days for fear of their getting a chill in the udder and consequent inflammation. It is very possible, therefore, that the lowness of the amount of fat in some samples of colostrum is attributable, at least in part, to this cause.

Ergel and Schlag (*Milchwirtschaft Forsch.*, 1924, **2**, 1) have given results for the colostrum of three cows which are in close agreement with those given above. They found the freezing-point to fall in some instances as low as —0·605°.

Cow No. 1

Jersey Cow—Bull Calf born 1 a.m., December 19th, 1933

Number	Day	Time	Fat Per Cent.	Solids-not-fat Per Cent.	Ash Per Cent.	Protein Per Cent.	Δ*
G.2528	1	7 a.m.	4·1	14·1	1·10	9·09	0·570
2529	1	2 p.m.	10·9	12·0	0·99	7·94	0·576
2530	1	5.15 p.m.	12·3	10·8	0·91	6·60	0·576
2534	2	7 a.m.	6·0	10·5	0·95	4·65	0·579
2535	2	2 p.m.	8·6	9·4	0·84	4·47	0·562
2536	2	5.30 p.m.	8·6	9·2	0·87	4·53	0·558
2541	3	7 a.m.	5·6	9·7	0·84	4·36	0·563
2542	3	2 p.m.	7·1	10·1	0·92	4·58	0·580
2543	3	5.30 p.m.	4·6	9·5	0·84	4·29	0·559

Cow No. 2

Friesian Cow—Calf born dead 5 a.m., December 18th, 1933

Number	Day	Time	Fat Per Cent.	Solids-not-fat Per Cent.	Ash Per Cent.	Protein Per Cent.	Δ*
G.2531	2	7 a.m.	1·3	21·9	1·20	17·46	0·590
2532	2	2 p.m.	1·7	19·1	1·18	14·53	0·582
2533	2	5.15 p.m.	3·5	16·7	1·12	12·12	0·572
2537	3	7 a.m.	7·2	13·2	1·04	8·92	0·569
2538	3	2 p.m.	14·0	11·3	0·95	—	0·558
2539	3	5.30 p.m.	15·2	11·1	0·87	7·93	0·557
2544	4	7 a.m.	4·1	9·3	0·92	4·10	0·549
2545	4	2 p.m.	5·3	9·1	0·84	—	0·560
2546	4	5.30 p.m.	4·3	9·0	0·87	4·12	0·541

*Δ is the depression of the freezing-point below that of water determined in the standard Hortvet apparatus.

Monier-Williams (*Food Report to the L.G.B.*, 1914, No. 22, p. 19) found for four samples of colostrum, depressions of 0·528°, 0·547°, 0·549° and 0·544°, respectively, but these, being corrected figures, will be about 0·014° smaller than figures obtained in the Hortvet apparatus.

The freezing-points recorded in this note were determined by my colleagues, Mr. Arnold Lees, F.I.C., and Mr. R. J. Taylor; the other results were obtained by my colleague, Mr. Neil Heron, A.I.C.

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Investigations into the Analytical Chemistry of Tantalum, Niobium, and their Mineral Associates

XXVII. Observations on Manganese, and the Analysis of Tantalite

BY W. R. SCHOELLER, PH.D., AND H. W. WEBB

(WORK DONE UNDER THE SOCIETY'S ANALYTICAL INVESTIGATION SCHEME)

MANGANESE is an essential constituent of the minerals of the isomorphous columbite-tantalite series, in which manganese and iron, as well as niobium and tantalum, replace each other in all proportions. The principal ore of tantalum is West Australian manganotantalite. Manganese figures as a subordinate constituent in certain earth-acid minerals. In accordance with the general plan followed in these investigations, we have studied the behaviour of manganese in tartrate solution. Observations were made on its precipitation, (A) as sulphide, and (B) as tannin complex. The concluding part of this section gives an outline of a new process for the analysis of tantalite and columbite, based on analytical methods published in this series of investigations.

A. PRECIPITATION AS SULPHIDE.—The precipitation of manganous sulphide from ammoniacal tartrate solutions is the subject of conflicting statements in the literature. It is generally understood that manganese is incompletely precipitated under such conditions (Hillebrand and Lundell, *Applied Inorganic Analysis*, New York, 1929, p. 60). Rüdisüle (Volume **5**, 436), on the other hand, states that tartaric acid does not interfere, while Rose even prescribes the precipitation as sulphide in presence of non-volatile organic compounds. He observes, however, that manganous sulphide is not altogether insoluble, especially in presence of ammonium salts, and that minute quantities do not settle out for a long time. Withey, describing a process for the analysis of aluminium, in which the metallic impurities are precipitated as sulphides from tartrate solution (*J. Inst. Met.*, 1916, **15**, 207), states: "Manganese in the process appears to behave in a curious manner, the causes for which have not been worked out. The larger portions, however, escape precipitation."

Our experimental work, briefly recorded below, confirms the singular behaviour of manganese in tartrate solutions. Preliminary tests were made with a solution prepared by reduction of a known amount of pure potassium permanganate with hydrochloric and sulphurous acids. Measured volumes of the solution were treated with tartaric acid and ammonium chloride as specified in the table below, made ammoniacal, and treated with freshly-prepared ammonium sulphide. After standing overnight in stoppered flasks, the flesh-coloured precipitates were filtered off and dissolved in dilute sulphuric acid, and the manganese in the solutions was determined gravimetrically as pyrophosphate. The metal was almost quantitatively recovered.

Exp.	$C_4H_6O_6$ Grms.	NH_4Cl Grms.	MnO taken Grms.	$Mn_2P_2O_7$ found Grms.	MnO found Grms.	MnO error
1	3	5	0·1000	0·2000	0·1000	0·0000
2	6	5	0·1000	0·1998	0·0999	—0·0001
3	6	8	0·0100	0·0196	0·0098	—0·0002
4	6	8	0·0050	0·0097	0·0048	—0·0002

Precipitation was instantaneous, except in Exp. 4, where it occurred after less than a minute.

Having proved that manganese is readily precipitated as sulphide in presence of relatively large amounts of tartaric acid, we proceeded to experiment with a manganotantalite concentrate assaying 10·60 per cent. of MnO. The fine powder (0·5 grm.) was fused with potassium bisulphate, and the melt was dissolved in tartaric acid solution. The liquid was saturated with hydrogen sulphide and filtered. The bulk of the earth acids was then eliminated by boiling with 30 ml. of strong hydrochloric acid; the manganese and iron were thus obtained in the filtrate from the hydrolysis precipitate. It was at the next stage—treatment of the ammoniacal tartrate solution with ammonium sulphide—that we experienced the erratic behaviour of manganese. In at least 20 experiments, in which we endeavoured to attain a quantitative precipitation, our manganese recoveries varied from almost *nil* to over 95 per cent.; but as we cannot definitely explain the cause of the variable results, no useful purpose would be served by describing the tests. We observed, however, that dilution tends to prevent precipitation. Following up this clue we were led to reduce the volume of our solutions, with the result that, at very high concentrations, we achieved almost quantitative recoveries. This expedient (for which we have no theoretical explanation, since it was unnecessary in Exps. 1 to 4) is applied in the process for the analysis of tantalite given below.

We proved that the bisulphate used in the tantalite tests is not responsible for the observed irregularities, by submitting pure manganous sulphate, as well as a high-grade pyrolusite, to bisulphate fusion; the manganese was readily precipitated as sulphide from the ammoniacal tartrate solution of the melt. Nor can the erratic behaviour of the metal be ascribed to the presence of the remaining small quantity of earth acid, since Withey (*loc. cit.*) observed it in the analysis of commercial aluminium, while Hillebrand and Lundell (*op. cit.*) make the general statement that the precipitation in ammoniacal tartrate solution does not "give a complete separation of manganese." The formation of a more or less stable tartaric manganese complex might be invoked, but this assumption cannot be reconciled with the fact that the solutions prepared from the pure manganese salts were readily precipitated in the tests already described. Having investigated the reactions of a number of elements in solutions containing tartaric or other organic acids, we have come to the conclusion that the present state of knowledge of the nature of such solutions is too imperfect to afford theoretical guidance in the problem under discussion.

B. PRECIPITATION BY TANNIN.—In Section XXIII (ANALYST, 1932, **57**, 551) Schoeller and Powell have classified the earth-forming elements into two analytical groups according to their behaviour towards tannin. Only the members of

Group A are precipitated from feebly acid oxalate solution half-saturated with ammonium chloride. Those of Group B are precipitated from neutralised tartrate solution containing alkali acetate. To these groups we may add a third, Group C, the members of which (manganese, beryllium, and the rare-earth metals) are precipitated by tannin from ammoniacal tartrate solution. The precipitates are readily soluble upon re-acidification of the liquid which holds them in suspension.

The manganese-tannin complex is colourless, or nearly so; when freshly precipitated it is pale grey in appearance, but on exposure to the air it darkens considerably; hence it turns brownish-black on the filter. The precipitation is practically quantitative. The hot tartrate solution is treated with ammonium chloride (10 grms.) and acetate (5 grms.), a fresh solution of 1 grm. of tannin (for 0·05 grm. of MnO), and a decided excess of ammonia. The liquid is allowed to stand overnight in the cold, and the precipitate is collected and washed with slightly ammoniacal 2 per cent. ammonium chloride solution containing a little tannin. It is always contaminated with silica; hence it is ignited and dissolved in hydrochloric acid, the solution is evaporated to dryness, the residue is dissolved in dilute acid, and the manganese in the filtered solution is determined as pyrophosphate.

Exp.	$KMnO_4$ Grms.	Equivalent to MnO Grms.	MnO found Grms.	Error
5	0·0617	0·0277	0·0272	—0·0005
6	0·1078	0·0484	0·0471	—0·0013

We wish to make it clear that we are not advocating the above procedure as a method for the determination of manganese; we merely record, by way of a contribution to the study of the behaviour of metals in tartrate solution, that manganese is precipitated therefrom by tannin and an excess of ammonia.

C. ANALYSIS OF TANTALITE (COLUMBITE).—It may be opportune in this Section to give an outline of our procedure for the determination of the major constituents of tantalite, as it includes the quantitative separation of the earth acids from manganese and iron. It has been perfected, and used for several years, in actual practice. We claim that it renders the time-honoured pyrosulphate hydrolysis process obsolete (*cf.* ANALYST, 1928, **53**, 467), at any rate for tantalite and columbite. The directions given below also replace those published in Section I (*id.*, 1922, **47**, 93) for the solution of the bisulphate melt of 1 grm. of mineral in a solution of 10 grms. of tartaric acid in not more than 50 ml. of water. In its present improved form the process enables us to carry out the analysis (including the separation of tantalum from niobium) on 0·25 grm. of material, or even less.

(*a*) *Decomposition and Solution.*—The mineral (0·5 grm.), ground to an impalpable powder, is fused in a silica crucible with 4 grms. of potassium bisulphate. The fused mass is spread against the side of the crucible; leaching is effected with 10 per cent. tartaric acid solution (40 ml.). The crucible is filled with moderately hot solvent, and allowed to stand for a short time. When the mass has become detached it is transferred to a squat 400-ml. beaker; the crucible is well rinsed with hot water and reserved. The liquid in the beaker (100 ml.) is stirred without interruption until the cake has disintegrated, leaving a pulverulent residue or precipitate which dissolves to a clear solution when the liquid is subsequently heated to incipient boiling during constant agitation. If this precipitate is allowed to settle, the particles begin almost at once to adhere to each other and to the bottom of the beaker; when dislodged they are no longer completely soluble, as they leave thin transparent pellicles of tantalic acid, which require re-treatment. With columbites, lixiviation of the melt is more easily effected.

(*b*) *Tin and Silica Fraction.*—The liquid is treated with 5 ml. of 10 per cent. sulphuric acid, and with a stream of hydrogen sulphide until cold. The beaker is left for a few hours in a warm place; a little creamed filter pulp is stirred in, and the solution is poured through a 9-cm. No. 40 Whatman paper into a 600-ml. beaker. The insoluble portion is collected and washed with acidulated hydrogen sulphide water, gently ignited in a porcelain crucible, and weighed as SnO_2 *plus* siliceous gangue; it is analysed as explained in Section XX (ANALYST, 1931, **56**, 800).

(*c*) *Major Earth-acid Fraction.*—The filtrate from the previous operation, containing hydrogen sulphide and the iron as ferrous salt, is heated to boiling and treated with 30 to 35 ml. of strong hydrochloric acid (XVI, *id.*, 1929, **54**, 704). After a few minutes' boiling the precipitate, *HP*, consisting of the great bulk of the earth acids free from iron and manganese, is left to settle, collected as described in Section XIX, E (*id.*, 1931, 308), washed with 2 per cent. hydrochloric acid, and ignited in the tared silica crucible previously used (*vide infra, e*).

(*d*) *Manganese Iron Fraction.*—The filtrate from *HP* is boiled down to small bulk in an 800-ml. beaker, and transferred to a 250-ml. beaker, in which it is evaporated to a volume of about 20 ml. The ferric salt in the solution is reduced by hydrogen sulphide gas, whereupon the liquid is treated with a decided excess of strong ammonia and 10 ml. of fresh ammonium sulphide. The precipitate, which contains the whole of the iron and usually all but 1 to 3 mgrms. of the manganese, is allowed to settle for some hours in a warm place, then collected on a 9-cm. No. 40 Whatman paper containing a pad of filter pulp in its apex, and washed with warm water containing ammonium sulphide and chloride.

The washed sulphide precipitate is ignited in a small porcelain dish, and dissolved in a few ml. of hydrochloric acid. After addition of 0·25 to 0·5 grm. of ammonium chloride the solution is evaporated to dryness. In our experience the crystalline residue always dissolves in cold water to a clear solution; hence it is free from earth acid. The chloride solution is transferred to a 400-ml. beaker, treated with ammonium acetate, diluted to about 150 ml., and heated to incipient boiling; the basic ferric acetate is collected, washed, and dissolved in hydrochloric acid, the iron is re-precipitated with ammonia, and the precipitate is ignited to Fe_2O_3. The filtrate from the basic acetate is treated with ammonium chloride and phosphate (Treadwell, 7th Ed., Vol. II, 133); the manganese precipitate is ignited to pyrophosphate.

(*e*) *Minor Earth-acid Fraction.*—The filtrate from the sulphide precipitate is slightly acidified with acetic acid, boiled until free from hydrogen sulphide, and treated while boiling with a fresh solution of 1 grm. of tannin (XVII, *id.*, 1929, 710). The coloured precipitate, *TP* (which is free from manganese, as proved by fusion with potassium carbonate), is coagulated on the water-bath, collected, washed (XIX, *loc. cit.*, 308) and ignited in the crucible containing *HP* (*vide supra, c*). The combined precipitates are leached as usual (XIX, 309), collected, ignited in the silica crucible, and weighed as M_2O_5. The precipitate is then fused with bisulphate, etc., for the separation of tantalum from niobium (XXIV, *id.*, 1932, **27**, 751).

(*f*) *Minor Manganese Fraction.*—The filtrate from *TP* contains a mgrm. or two (sometimes more) of manganese. We find it best to boil it down with a large excess of nitric acid and 10 ml. of sulphuric acid, for the destruction of the tannin, tartaric acid and ammonium salts. The final acid mass, which should be quite colourless, is diluted and tested colorimetrically for manganese, *e.g.* by means of persulphate in presence of silver nitrate.

SUMMARY.—Ammoniacal tartrate solutions of pure manganous salt were found to be readily precipitated by ammonium sulphide. On the other hand, the ammoniacal tartrate solutions obtained in the analysis of manganotantalite, when submitted to the same treatment, were incompletely precipitated—in a few of the tests hardly at all. An almost quantitative precipitation of manganous sulphide was, however, achieved after previous evaporation of the solutions to very small volume. No theoretical explanation for this erratic behaviour suggests itself. Manganese is precipitated from tartrate solution by tannin and an excess of ammonia. The precipitation is practically quantitative. A new process for the analysis of tantalite is described; it is based on the analytical methods elaborated in the course of these investigations.

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A Note on the Taka-diastase Method for Determining Starch

BY J. J. CHINOY, M.SC., F. W. EDWARDS, F.I.C., AND H. R. NANJI, PH.D., D.I.C., A.I.C.

VARIOUS investigators working on the determination of starch, especially in materials such as apples (*cf.* Widdowson, *Ann. Bot.*, 1932, **46**, 597) and some cereals, have recorded the extreme difficulty of extracting the starch completely. In addition to water, solutions of various salts, such as calcium chloride, have been tried for extraction of the starch, but with comparatively little success.

Reychler (*Bull. Soc. Chim. Belg.*, 1920, **29**, 118) was the first to show that starch is rapidly gelatinised by solutions, as weak as 0·7 per cent., of sodium or potassium hydroxide. It was therefore considered desirable to study the effect, if any, of alkali gelatinisation in the taka-diastase method of determining starch, making provision, of course, for the adjustment of the solution to the right p_H prior to the action of the taka-diastase. The method we adopted for the subsequent determination of mixed reducing sugars obtained by the taka-diastase hydrolysis of starch was that of Widdowson (*Biochem. J.*, 1931, **25**, 863); this method was considered to be satisfactory for the purpose in view, as it is applicable to the determination of small quantities.

The preliminary experiments were carried out with pure potato starch, and the method finally adopted was as follows:

A weighed quantity (0·5 grm.) of potato starch (dried *in vacuo* at 120° C. for 3 hours) was gelatinised with about 80 ml. of 0·7 per cent. potassium hydroxide solution by warming at 60° to 70° C. on a water-bath for half an hour. The solution was cooled to room temperature and made up to 100 ml. in a graduated flask. An aliquot portion (about 50 ml.) was treated in a conical flask with the exact quantity of 5 per cent. acetic acid required to neutralise the alkali.* The solution was made slightly acid by the addition of 0·1 ml. of 5 per cent. acetic acid, 10 ml. of 0·1 per cent. solution of taka-diastase and a little toluene were added, and the flask was incubated at 37° C. for half an hour.† The liquid was then boiled for a minute to arrest the activity of the enzyme, cooled to room temperature, and made up to a known volume. The reducing sugars, glucose and maltose, were then determined in aliquot portions‡ by the method laid down by Widdowson (*loc. cit.*), and the amount of starch calculated.§ Our results have shown that over 99 per cent. of the starch was accounted for.

The application of the use of alkali gelatinisation to the determination of starch in leaves, apples, potatoes, etc., is now in process of investigation.

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* This was determined on a separate 10 ml.-portion of the solution, phenolphthalein being used as indicator.

† In our experiments the hydrolysis was complete in 5 to 10 minutes; completion of hydrolysis can be ascertained with a drop of iodine solution.

‡ Widdowson (*loc. cit.*) suggested that an aliquot portion should contain about 3 mgrms. of reducing sugars.

§ We are, of course, aware of the findings of Horton (ANALYST, 1921, **46**, 456), but Widdowson (*loc. cit.*), who refers to Horton's work, has shown that if pure starch, which has been properly dried, is hydrolysed with freshly prepared 1 per cent. taka-diastase solution under the conditions specified in her paper (which we have followed), between 99·2 and 99·7 per cent. of starch could be accounted for. We have confirmed her results.

A New Iodine Method for the Determination of Starch

BY J. J. CHINOY, M.SC., F. W. EDWARDS, F.I.C., AND H. R. NANJI, PH.D., D.I.C., A.I.C.

Part I. Soluble Starch

WHILST a considerable number of methods have been put forward, from time to time, for the determination of starch, so far none has been found satisfactory in all cases. The methods may be classified into: (i) polarimetric; (ii) saccharimetric; (iii) gravimetric; (iv) specific-gravity methods; and (v) iodine methods.

A very complete account of all the above classes is given by Walton (*A Comprehensive Survey of Starch Chemistry*, Vol. I, p. 143, *et seq.*). In this series of publications we are concerned only with the fifth type, *viz.* the iodine methods.

Opinion still varies regarding the chemical nature of the compound of starch with iodine. One school of thought considers that starch forms a definite series of chemical compounds with varying proportions of iodine in the molecule. Later work of Berczeller (*Biochem. Z.*, 1922, **133**, 502), Lottermoser (*Z. angew. Chem.*, 1924, **37**, 845), and especially of Dhar (*J. Physical Chem.*, 1924, **28**, 125), appears to show definitely that mere adsorption compounds of iodine with starch are formed. Whatever may be the chemical nature of the starch iodide formed, it was shown quite early by Stocks (*Chem. News*, 1887, **56**, 212; 1888, **57**, 183) that the colloidal starch iodide could be readily precipitated from the solution by alcohol, dilute acids, and certain inorganic and organic salts. He also showed that the starch iodide precipitate was not affected by alcohol, ether, benzene, and other organic solvents.

A number of volumetric iodimetric methods have been published (for a summary see Walton, *loc. cit.*, p. 168) for the determination of starch. They depend either upon measuring the iodine taken up by the starch, or on the determination of iodine in the starch iodide precipitate. Methods of the first type are obviously of no use where starch occurs with other substances which react with iodine, and their use is restricted to pure starches. Methods of the second type also appear to give discordant results, owing to the difficulty of removing free iodine.

The gravimetric iodine methods of starch determination were based on the observations of Stocks (*loc. cit.*), but in nearly all cases the starch iodide was either reconverted into starch and weighed as such (*cf.* Kaiser, *Chem.-Ztg.*, 1902, **26**, 180; Fellenberg, *Chem. Zentr.*, 1917, **1**, 450), or hydrolysed to dextrose and the sugar determined polarimetrically (*cf.* Small, *J. Amer. Chem. Soc.*, 1919, **41**, 107).

No attempt, so far as the authors are aware, has been made to standardise the conditions of precipitation of starch iodide and to weigh it as such. It was anticipated that, if strict conditions of procedure were followed, the obvious difficulty of the formation of various types of adsorption compounds could be overcome. This expectation was well borne out by experiments, which are described later.

Observations were first carried out with soluble starch, A.R. This was dried at 120° C. in a vacuum for 3 hours. It was found that this was the best method of drying all the starches in a comparatively short time. The method, in general, consisted in dissolving a weighed quantity of dry starch in boiling water, adding an excess of iodine, precipitating the colloidal starch iodide by various reagents, filtering off the starch iodide precipitate on a tared alundum crucible, washing the precipitate with alcohol, drying for a fixed time at 100° C., weighing the starch iodide precipitate, and from this weight calculating the amount of starch by the use of a factor. This factor was ascertained by determining the weight of starch iodide from a weighed quantity of different pure starches. It was found that the amount of starch in solution is obtained from the weight of starch iodide by multiplying by the factor 0·8865.

Owing to the difficulty of complete extraction of starch from various plant materials by water, etc. (see page 671), it was considered desirable to apply the method after alkali gelatinisation. Also, as alcohol could not be used as a coagulating agent in all cases (for example, in substances in which starch occurs together with pectins), it was necessary to try other coagulating agents, such as dilute acids and certain salts. A detailed account is given in the experimental section.

Preliminary observations showed that, whatever coagulating agent is used, it is essential to adhere strictly to (i) and (iv) of the following conditions:

(i) *Quantity of iodine.*—An excess of iodine must be used, as then the degree of adsorption of iodine by starch is constant.

(ii) *Time of contact of iodine with starch.*—This has little effect, as the adsorption compound is formed within the first minute if excess of iodine is present.

(iii) *The quantity of coagulating agent.*—This has to be determined in preliminary experiments. Its nature and use are fully discussed in the experimental section.

(iv) *Degree of washing.*—This has some slight effect, and, therefore, a fixed quantity (200 ml.) of alcohol is used.

EXPERIMENTAL

ALCOHOL USED AS COAGULANT.—The dried soluble starch (0·5 grm.) was dissolved in 100 ml. of boiling distilled water, and the solution was cooled to room temperature. To 10 ml. of the cooled solution, 1 ml. of *N*/10 iodine solution was added and, after a minute, 20 ml. of rectified spirit,* with stirring. The starch-iodide was coagulated at once and settled down in about 5 minutes. After that time the precipitate was filtered off on a tared alundum crucible (Gooch crucibles with asbestos were not found quite satisfactory), washed with 200 ml. more of rectified spirit, dried in the oven at 100° C. for 12 hours, and weighed. The results are tabulated below.

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* A point to be noted with regard to all the coagulating agents used in this investigation is that they are to be added after the iodine, otherwise imperfect precipitation results.

TABLE I

Precipitation with Alcohol

Volume of 0·5 per cent. starch solution taken Ml.	Weight of starch iodide (A) Grm.	Weight of starch found (A × 0·8865) Grm.	Weight of starch taken Grm.
10	0·0562	0·0499	0·0500
10	0·0564	0·0500	
10	0·0559	0·0496	
25	0·1414	0·1253	0·1250
25	0·1412	0·1251	
25	0·1412	0·1251	
50	0·2825	0·2504	0·250

COAGULATION WITH SULPHURIC ACID.—To 10 ml. of the 0·5 per cent. starch solution (used above), 1 ml. of $N/10$ iodine solution was added, followed by 1 ml. of 25 per cent. H_2SO_4. After keeping for 5 minutes the precipitate of starch iodide was filtered in a tared crucible and washed* with 200 ml. of rectified spirit, dried at 100° C. for 12 hours and weighed.

With this coagulant it was found to be important to wash the precipitate thoroughly, otherwise high results were obtained. The results are tabulated below in Table II.

TABLE II

Precipitation with Sulphuric Acid

Volume of 0·5 per cent. starch solution taken Ml.	Weight of starch iodide (A) Grm.	Weight of starch found (A × 0·8865) Grm.	Weight of starch taken Grm.
25	0·1410	0·1249	0·1250
25	0·1494	0·1320 *	
25	0·1412	0·1251	
10	0·0562	0·0499	0·050
10	0·0568	0·0503	

* Insufficient washing.

COAGULATION WITH HYDROCHLORIC ACID.—The procedure was identical with that used with sulphuric acid, 1 ml. of dilute hydrochloric acid (1 part of concentrated hydrochloric acid : 1 part of water) being used for 10 ml. of the solution. The results, however, were low in each case, showing that the hydrochloric acid had some hydrolysing action on starch iodide. This was confirmed by our obtaining increasingly low results with increasing quantities of the acid. The results are tabulated below.

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* A quicker method of washing the precipitate free from sulphuric acid is to carry out the precipitation in a centrifuge tube. The liquid, after precipitation, is centrifuged and carefully decanted. Alcohol is then added and the precipitate thoroughly mixed; the liquid is again centrifuged and decanted. The washing with alcohol is repeated three times.

TABLE III

Precipitation with Hydrochloric Acid

Volume of 0·5 per cent. starch solution taken Ml.	Volume of 50 per cent. HCl added Ml.	Weight of starch iodide (A) Grm.	Weight of starch found (A × 0·8865) Grm.	Weight of starch taken Grm.
25	0·5	0·0978	0·0867	0·1250
25	0·5	0·0973	0·0863	
25	1·0	0·0944	0·0837	
25	3·0	0·0914	0·0810	
25	5·0	0·0906	0·0803	

COAGULATION WITH POTASSIUM ACETATE SOLUTION.—As alcohol and dilute acids are known to precipitate hemicelluloses and other polysaccharides with which starch often occurs, their use is limited. It was necessary, therefore, to use some neutral salt as a coagulating agent. A 10 per cent. solution of potassium acetate was chosen and found most satisfactory, because, as it is one of the rare neutral salts freely soluble in alcohol, the excess could be readily washed out.

The determination is carried out exactly as in the preceding experiments, 2 ml. of 10 per cent. potassium acetate solution being used with 10 ml. of 0·5 per cent. starch solution. The results are tabulated below.

TABLE IV

Precipitation with Potassium Acetate Solution

Volume of 0·5 per cent. starch solution taken Ml.	Volume of potassium acetate solution added Ml.	Weight of starch iodide (A) Grm.	Weight of starch found (A × 0·8865) Grm.	Weight of starch taken Grm.
10	2	0·0559	0·0496	0·050
10	2	0·0564	0·050	
10	2	0·0562	0·0499	
10	4	0·0568	0·0505	
10	4	0·0569	0·0504	

GELATINISATION OF STARCH WITH ALKALI.—Dry soluble starch (0·5 grm.) was dissolved by warming with 0·7 per cent. potassium hydroxide solution at 60° to 70° C. on a water-bath for 30 minutes. After cooling, starch was determined in an aliquot portion by just neutralising with dilute acetic acid (phenolphthalein as indicator), and adding 1 ml. of $N/10$ iodine solution, followed by the coagulating agent. As alkali was used with the main purpose of meeting those cases in which starch is difficult to extract, as for example, cereals, and as these also contain pectic substances and hemicelluloses, the best coagulating agent would evidently be potassium acetate, some of which is already formed by neutralisation of the potassium hydroxide with acetic acid. Thus, potassium hydroxide solution answers best as a solvent for starch. A further 2 ml. of 10 per cent. potassium acetate solution is added to complete the precipitation. After standing for 5 minutes the precipitate is treated and weighed as described on p. 674.

It may be added that when hemicelluloses and other interfering substances are absent, alcohol and dilute sulphuric acid could be used for coagulation, with perfectly satisfactory results. The results are tabulated below.

TABLE V

Volume of starch solution Ml.	Coagulating agent	Weight of starch iodide (A) Grm.	Weight of starch found (A × 0·8865) Grm.	Weight of starch taken Grm.
10	25 ml. alcohol	0·0564	0·0500	
10	,,	0·0568	0·0503	
10	,,	0·0570	0·0504	
10	2.0 ml. potassium acetate solution	0·0560	0·0498	0·050
10	,,	0·0559	0·0496	
10	,,	0·0559	0·0496	

Part II. Natural Starches and Flour

The determination of starch in commercial flours affords useful information both to the miller and to the food chemist. Gerum (*Z. Unters. Nahr. Genussm.*, 1919, **37**, 145) discovered that the amount of starch in a flour also serves as a guide to its milling grade. Jacobs and Rask (*J. Ind. Eng. Chem.*, 1920, **12**, 899) discussed in great detail the importance of the determination of starch to a flour-mill chemist. They pointed out that the amount of starch contained in wheat flour or any similar milled product is a measure of the amount of the inner endosperm, which is the region of the seed yielding ordinary flour, there being no starch either in the bran tissue (including the aleurone layer) or in the embryo. Lintner (*Z. angew. Chem.*, 1911, **24**, 156), working on barley, also recommended the determination of starch as a method of valuation.

The methods at present adopted for the determination of starch in commercial flours and similar products are:

(i) Ewer's polarimetric method; (ii) O'Sullivan's diastase method (*J. Chem. Soc.*, 1884, **45**, 1).

Neither of these is expeditious or very accurate. We have therefore extended the gravimetric method of starch determination, described in Part I, to pure natural starches, as well as to some commercial flours. A noteworthy feature of the method is that it renders preliminary treatment, such as that for the removal of sugars, unnecessary.

The method was applied to four microscopically pure* varieties of natural starches,† *viz.* potato, maize, rice, and wheat. It was soon found that gelatinisation with water alone of the starches, even in the pure condition, occurred with some difficulty, especially in the case of rice starch. Several hours boiling with water was necessary to gelatinise the starch completely. We therefore abandoned gelatinisation with water and used 0·7 per cent. potassium hydroxide solution (in which the hemicelluloses in maize, rice and wheat starches are not appreciably soluble) throughout the course of the experiments, the further details of procedure being identical with those given on p. 676.

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* This term is used to indicate that there was no obvious adulteration of one starch with another.

† These four varieties represent a fair range of sizes of starch grains commonly met with: potato starch 25–75μ, wheat starch 20–35μ, maize starch 12–18μ, and rice starch about 6μ.

In the range of commercial flours we have applied the method to the two commonest varieties—wheat flour and rice flour. It is obvious that the same method could be applied to whole grains, which should be ground very finely in a Maercker mill and the whole powder then thoroughly mixed.

EXPERIMENTAL

PURE POTATO STARCH.—Potato starch was determined after gelatinisation with both water and 0·7 per cent. potassium hydroxide solution, and it was found to be the only variety of starch with which we worked that gave rapid and satisfactory gelatinisation with water alone. The results are tabulated below in Table VI. Series I gives results obtained with water gelatinisation, and Series II those with alkali gelatinisation. The results are strikingly in agreement in both cases.

TABLE VI

Pure Potato Starch in 0·5 per cent. Solution

Quantities of solution Ml.	Coagulating agent	Weight of starch iodide Grm.	Weight of starch found (A × 0·8865) Grm.	Weight of starch taken Grm.
Series I				
10	25 ml. alcohol	0·0558	0·0495	
10	,,	0·0562	0·0499	
10	,,	0·0558	0·0495	
10	,,	0·0558	0·0495	
10	1 ml. 25 per cent. H_2SO_4	0·0558	0·0495	0·050
10	,,	0·0557	0·0494	
10	1 ml. 10 per cent. potassium acetate	0·0562	0·0499	
10	,,	0·0560	0·0497	
Series II				
10	25 ml. alcohol	0·0558	0·0495	
10	,,	0·0560	0·0497	
10	,,	0·0560	0·0497	
10	,,	0·0562	0·0499	0·050
10	,,	0·0560	0·0497	
10	,,	0·0562	0·0499	
10		0·0568	0·0504	

PURE RICE STARCH.—On attempting to determine starch in a sample of microscopically pure rice starch by the method successfully employed with potato starch, we noticed some important differences:

(i) Gelatinisation with water was useless, as after 2 hours' heating a considerable quantity of insoluble powder remained behind.

(ii) With 0·7 per cent. potassium hydroxide solution, the gelatinisation was satisfactory, but the coagulation with alcohol or potassium acetate solution was not satisfactory unless filtration was carried out after leaving the mixture overnight. The results are shown in Table VII.

Series I represents results when the starch iodide was filtered immediately after precipitation, the low figures obtained being due to incomplete coagulation.

Series II represents results of filtration after keeping overnight.

TABLE VII

Pure Rice Starch in 0·5 per cent. Solution

Quantities of solution Ml.	Coagulating agent	Weight of starch iodide (A) Grm.	Weight of starch found (A × 0·8865) Grm.	Weight of starch taken Grm.
Series I				
10	25 ml. alcohol	0·0512	0·0454	0·050
10	,,	0·0517	0·0458	
10	1 ml. 10 per cent. potassium acetate	0·0515	0·0456	
10	,,	0·0520	0·0461	
Series II				
10	25 ml. alcohol	0·0562	0·0499	0·050
10	,,	0·0559	0·0496	
10	1 ml. 10 per cent. potassium acetate solution	0·0558	0·0495	
10	,,	0·0559	0·0496	

PURE MAIZE STARCH.—With maize starch, also, alkali gelatinisation alone was satisfactory; the coagulation of starch iodide, however, was quite satisfactory both with alcohol and with 10 per cent. potassium acetate solution, and there was no need to keep the solution overnight.

TABLE VIII

Pure Maize Starch

Quantities of solution Ml.	Coagulating agent	Weight of starch iodide (A) Grm.	Weight of starch found (A × 0·8865) Grm.	Weight of starch taken Grm.
10	25 ml. alcohol	0·0557	0·0494	0·050
10	,,	0·0557	0·0494	
10	,,	0·0558	0·0495	
10	,,	0·0559	0·0496	
10	1·0 ml. potassium acetate	0·0559	0·0496	
10	,,	0·0557	0·0494	

PURE WHEAT STARCH.—A microscopically pure wheat starch was gelatinised with 0·7 per cent. alkali (water gelatinisation was unsatisfactory), and the starch was determined as before.

TABLE IX

Pure Wheat Starch

Quantities of solution Ml.	Coagulating agent	Weight of starch iodide (A) Grm.	Weight of starch found (A × 0·8865) Grm.	Weight of starch taken Grm.
10	25 ml. alcohol	0·0564	0·050	0·050
10	,,	0·0561	0·0498	
10	,,	0·0559	0·0496	
10	1 ml. 10 per cent. potassium acetate	0·0561	0·0498	
10	,,	0·0559	0·0496	
10	,,	0·0559	0·0496	

DETERMINATION OF STARCH IN COMMERCIAL FLOURS.—Three grms. of the flour (dried as on p. 674) were gelatinised with about 300 ml. of 0·7 potassium hydroxide solution at 90° C. in a water-bath for half an hour, and the solution was cooled to room temperature and made up to 500 ml. The liquid was filtered and the starch determined in an aliquot portion both by the starch iodide method and by Widdowson's taka-diastase method, as described on p. 672.

There is a fair agreement between the results obtained by the two methods, although with the taka-diastase method they are a trifle low.

TABLE X

Starch in Flours

Variety of flour	Starch found (by starch-iodide method) Per Cent.	Starch found (by taka-diastase method) Per Cent.
1. Wheat flour	71·5	71·2
2. ,,	73·5	72·2
3. ,,	73·8	73·5
4. Rice flour	78·6	78·0
5. ,,	79·9	79·15
6. ,,	74·5	74·0

The method adopted here for wheat and rice flours should be equally applicable to other commercial flours.

CONCLUSIONS.—It is evident that the gravimetric method of determining starch now evolved is both rapid and accurate and lends itself to several applications. It is of particular importance in food chemistry, for which the need of a rapid and accurate method for determining starch has been felt for a considerable time. The use of the method is therefore being further investigated with regard to its application to foodstuffs generally, both to those naturally containing starch and to those adulterated with it.

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The Accuracy of Biological Estimations of Vitamins

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VARIOUS papers have been published from the laboratories of the Pharmaceutical Society dealing with the accuracy obtainable there in biological estimations of the vitamins. The results have been stated in different ways for different purposes, and it now seems desirable to collect the results and express them all in the same form so that they may to some extent be compared.

A very short explanation of the methods by which these results have been calculated may be given.

THE STANDARD DEVIATION.—The "standard deviation" (S.D.) is perhaps the most generally used form of expressing the accuracy of a biological test. This expression (σ) denotes the limits within which two-thirds of the observations made under the same conditions may be expected to lie. Two-thirds of σ ("probable error") gives the limits within which half the observations will lie. Twice σ gives the limits within which 21/22 of the observations will lie. For example, it was found that in the breeding stock of normally growing rats of this laboratory, the average increase in weight of 237 female rats during the five weeks' period from the seventh to the twelfth week of life, was 45·9 grms. (M). The standard deviation of this result was obtained by finding the difference between the mean and each observation, squaring each difference, summing the squares, dividing the sum of the squares by the number of observations minus 1 and then taking the square root of the answer $\left\{\sigma = \sqrt{\frac{\Sigma d^2}{n-1}}\right\}$. It ($\sigma$) was found to be 9·59. Then, according to the theory of probabilities:

1/2 of the observations should lie within M ± 2/3 σ,
i.e. 45·9 ± 2/3 of 9·6
i.e. between 52·3 and 39·5

2/3 of the observations should lie within M ± σ
i.e. within 45·9 ± 9·6
i.e. within 55·5 and 36·3

21/22 of the observations should lie within M ± 2 σ
i.e. within 45·9 ± 2 × 9·6
i.e. within 65·1 and 26·7

The observations actually found within these limits are collected in Table I.

TABLE I

Distribution of observations on the increase in weight of female rats in a normal colony, from the 7th to the 12th week of life.

No. of observations, *i.e.* No. of rats = 237
Mean increase in weight (M) = 45·9 grms.
S.D. of mean increase in weight, σ = 9·59

		Calculated	Found
No. of observations within M ± 2/3 σ	..	118·5	127
No. of observations within M ± σ	..	158·0	163
No. of observations within M ± 2 σ	..	226·2	226

There is very good agreement between the calculated and found values· though the number of observations is only 237, and, indeed, we have often found good agreement in other sets of figures when the number of observations has been as small as 50. Someone unknown has remarked, "Everybody firmly believes in it (the normal law of errors), because the mathematicians imagine that it is a fact of observation, and observers that it is a theorem of mathematics."

It is a little more complicated to obtain a reliable value for the standard deviation of the increase in weight (in, say, 5 weeks) of rats which, having ceased to grow on a diet deficient in vitamin *A*, are then given a daily dose of some substance containing vitamin *A*. The standard deviation of the increase in weights of male rats is greater than that of female rats for similar periods. Thus the two sexes should be calculated separately. The standard deviation of small groups of rats in different tests will be found to vary greatly, and what is wanted for calculation of accuracy is a figure approaching the true standard deviation of the observation. This can be obtained by averaging the standard deviations of as many groups of results (tests) as possible; but a rather more accurate value (and, where the number of tests is large, not a very different value), may be found by summing all the squares of the deviations from the different means of the different tests, dividing by the total number of observations (N = No. of rats) minus the number of means (m = No. of tests) and taking the square root $\left\{\sigma = \sqrt{\frac{\Sigma d^2}{N-m}}\right\}$. This was done by Coward (1932) for the increase in weight—in 5 weeks—of rats which had ceased to grow on a diet deficient in vitamin *A*, and were then given a dose of some substance containing vitamin *A*. The values found for σ from 108 tests in which an average of 6 bucks and 7 does were used in each test were 14·72 for the bucks and 11·02 for the does. An analysis of the results showed that the standard deviation did not vary with variations in the mean increase in weight of groups of rats on different doses of vitamin *A*.

Later (1933), when results from a further 80 tests were available, the values for σ were found to be 15·37 for the bucks and 11·93 for the does.

The larger the number of animals from which a value for σ is calculated, the more nearly will this value approach the true value of σ. Calculations based on relatively small numbers of animals may be much below, or much above, the true value.

THE STANDARD ERROR.—The Standard Error of an average result which was obtained with a certain number of animals gives the limits within which, 2 out of

3 times, would lie the results of similar experiments made on the same numbers of animals. It is obtained by dividing the standard deviation by the square root of the number of animals used in the test, *i.e.* $\epsilon = \frac{\sigma}{\sqrt{n}}$. The probable error of the mean is $2/3\,\epsilon$.

THE USE OF THE STANDARD ERROR IN DETERMINING THE ACCURACY OF A TEST.—The accuracy of a test depends not only on the standard deviation of the response, but also on the slope of the curve relating response to dose of vitamin given. To find the degree of accuracy indicated by a certain standard deviation, the abscissae (doses of vitamin) corresponding to M and M ± σ, respectively, are determined either directly from the curve of response or by calculation from the equation of the curve of response. The range of values thus obtained is expressed as a percentage of the abscissa (dose) corresponding to the mean increase.

The figures in Table II, giving approximately the degrees of accuracy obtainable in the laboratories of the Pharmaceutical Society for various tests, have been calculated by the method just described. Fuller information on these results may be obtained by consulting the original papers (see list of references).

The curves of response for vitamin *A*, B_1 (rats) and *D* are logarithmic, those for B_1 (pigeons) approach the logarithmic shape somewhat, but the curve for vitamin *C* is a straight line. Hence the accuracy obtainable in tests for vitamins *A*, B_1 (rats) and *D* is independent of the size of the result, *i.e.* the result has the same accuracy whether it is a large or a small one. The accuracy of B_1 (pigeons) results is almost independent of the size of the result, but very high results should be regarded with suspicion and the experiment repeated with lower doses. The accuracy of a vitamin *C* result varies with the size of the result, for, the curve of response being a straight line, the standard deviation gives a higher percentage error on a low result than on a high one. We have evidence from 52 tests that there is no less variation in the low responses than there is in the high; thus there is no low value for the standard deviation of low results to compensate for this.

COMPARISON OF TWO SUBSTANCES (*e.g.* AN UNKNOWN WITH THE STANDARD).—The figures in Table II refer to the accuracy obtainable with a single group of 10 rats. Results from a single group of rats are, however, of little value, especially in vitamin tests where the response of a group of animals to the same dose of vitamin is known to fluctuate to an alarming extent. (Bourdillon *et al.*, 1931; Coward and Key, 1933, Vitamin *D*; and Coward, Key and Morgan, 1933, Vitamin *A*.) Thus the need for a simultaneous test on a standard of reference is obvious. (The standards available for vitamin tests are described in the Report of the Permanent Commission on Biological Standardisation, League of Nations, Health Organisation, 1931.) This introduces a second source of inaccuracy, for the result on the standard may be inaccurate as well as the result on the unknown. To measure the inaccuracy of a comparison of two substances (*i.e.* the inaccuracy of the potency of one relative to the other), the S. D. (σ) of the response is multiplied by $\sqrt{2}$, and the range so obtained interpreted as range of dose just as in the interpretation of the standard deviation. Results so obtained are collected in Table III, the "probable error" (the most usual form) of the estimation being given.

COMPARISON WITH CALCULATIONS OF OTHER WORKERS.—A summary of the calculations by other workers of their errors in estimation of vitamin *D* has been given by Coward and Key, 1933. Bourdillon *et al.* claim a probable error of +12 per cent. in a comparison of 2 substances by the use of 10 pairs of rats, estimating healing by the *X*-ray method. The "ash content of the bones" method had a probable error of about 20 per cent. for 10 pairs of rats for a range of doses of 0·03 to 0·64 unit (Hume, Pickersgill and Gaffikin, 1932; Bourdillon and Bruce, 1932). Morgan obtained a probable error of about 9 per cent. by the use of 10 pairs of rats, though his calculation was made on an admittedly small number (200) of rats. Bills made a calculation, by a somewhat unorthodox method, from his results, and claimed a probable error of about 20 per cent. when 10 pairs of rats were used. Thus the accuracy of the tests reported in this paper is very similar to that reported by other workers. There is no information from other laboratories on the accuracy of tests for other vitamins.

TABLE II

The accuracy of determination from 10 animals in various vitamin tests.

Each pair of figures gives the limits (as per cent. of true result) within which the experimental result will, with a known probability, lie

	Vitamin *A*				Vitamin B_1			Vitamin *C*	Vitamin *D*
	3 weeks' test		5 weeks' test		Rats	Pigeons			
	♂	♀	♂	♀		Percentage cured	Duration of cure		
1/2 chance	121	130	117	124	106	125	131	114	112
(probable error)	82	77	85	80	95	79	73	86	89
2/3 chance	134	147	128	138	109	145	148	122	120
	74	67	78	73	92	71	65	78	84
21/22 chance	180	222	163	191	119	282	216	145	144
	56	45	61	53	84	52	45	55	70
No. of observations (*i.e.* animals) from which each calculation was made ..	1014	1187	960	1100	119	325	187	234	1213

The curves relating response to dose of vitamin *A*, B_1 (rats) and *D* are logarithmic.

The curves relating response to dose of Vitamin B_1 (pigeons) are not logarithmic; therefore, the errors have been calculated for (*a*) 50 per cent. of birds cured, and (*b*) an average of 4 days' cure.

The curve relating protection from scurvy to dose of vitamin *C* is a straight line. The errors in the estimation of this vitamin have been calculated on a moderate amount of protection from scurvy, *i.e.* on the figure 2·0 in a scale where 0 represents "no protection" and 4 represents "complete protection" from scurvy.

TABLE III

Probable error of comparison of 2 substances, *e.g.* a substance of unknown potency and the standard of reference when 10 animals are used for testing each substance

Test	Probable error of estimation Per cent.
Vitamin *A*, 5 weeks' test (bucks)	+25 or −20
,, ,, ,, (does)	+47 or −32
Vitamin *A*, 3 weeks' test (bucks)	+31 or −24
,, ,, ,, (does)	+57 or −36
Vitamin B_1, 3 weeks' test (rats)	+ 9 or − 8
,, pigeons, percentage cured	+44 or −30
,, ,, duration of cure	+43 or −34
Vitamin *C*	±20
Vitamin *D*	+19 or −17

CONCLUSION.—Biological tests for vitamins are exceedingly sensitive. If we assume that the vitamin *D* of cod-liver oil and of butter is actually calciferol, then an amount of calciferol as small as 0·0001 mgrm. can be detected in any weight of cod-liver oil, butter or other foodstuff that can be given to a rat over a period of 10 days. Thus the concentration of vitamin *D* in cod-liver oil may be 1 in 200,000 parts and in butter it may be 1 in 40,000,000 parts. In other foodstuffs it is less.

The inaccuracy of biological tests for vitamins is great and apparently inevitable. It may, however, be claimed that it is no greater than that of biological tests for many other substances. A measure of this inaccuracy prevents the making of false comparisons by concluding that two results are different when indeed they are not, and it gives a known amount of confidence in results which one might otherwise be inclined to reject from a general distrust of biological tests.

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Notes

The Editor wishes to point out that the pages of the Journal are open for the inclusion of short notes dealing with analytical practice and kindred matters. Such notes are submitted to the Publication Committee in the usual manner.

IDENTIFICATION OF GLASS SPLINTERS

In the year 1933 the problem of identifying certain minute splinters of glass relating to a charge of theft was referred by the Police to the Dominion Laboratory, New Zealand. The splinters were found slightly embedded in one corner of the attaché case of an accused, who, it was alleged, had used the case to break a shop window preparatory to taking goods. A piece of plate glass taken from the edge of the hole in the window, together with sweepings containing glass from the police cell in which the accused was placed, was also forwarded by the Police. The specimens were examined with regard to refractive index, appearance under ultra-violet light and specific gravity. In addition to the specimens, other samples of glass of various types (including plate-, window-, bottle-glass, etc.), obtained from merchants and elsewhere, were examined for comparison.

For the determination of the refractive index the shadow or Van-der-Kolk method was used (Larsen, *Microscopic Determination of Non-opaque Minerals*, U.S. Dept. of Interior, Geological Survey Bull. 679; Smith, *Minerals and the Microscope*, Murby & Co., London). The specimen to be examined (of pin's-head size in these cases) was covered completely, on the microscope slide, with a liquid of known refractive index, and viewed under an objective by means of transmitted monochromatic (sodium) light with even illumination of moderate power. Part of the field was shaded by placing a card beneath the stage. With this instrument, when the refractive index of a test specimen was lower than that of the liquid, a dark border was observed on the side of the specimen towards the shadow in the field and a bright border on the opposite side. When the refractive index of a specimen was higher than that of the liquid the phenomena were reversed. Confirmation was obtained by Becke's test of raising and lowering the microscope tube and observing the contraction and expansion of the ring of light around the specimen; thus, if the specimen was of higher refractive index than the liquid, the ring of light contracted on raising the tube. The refractive indices of the liquids were checked by the refractometer when necessary. With a sufficient range of liquids (prepared, if necessary, by using mixtures), it was found that the refractive index of a specimen could be narrowed down to within 0·002 of its value, when the specimen became practically invisible. After approximate classification the final determinations were made at constant temperature. The refractive indices of the glass from the attaché case and that from the broken window were found to be similar (*viz.* 1·532), but that of the glass from the police cell was somewhat lower. This was also confirmed by observing all three specimens together on the same slide. Of twenty-two other specimens of glass examined for refractive index, four had values closely approximating or equal to 1·532, whilst 12 had a lower, and 6 a higher value.

The specimens were also examined under the microscope in ultra-violet light, a large flask filled with water being used as a condenser. It was hard to compare, macroscopically, large samples fluorescing somewhat similarly, but the examination of splinters under the microscope facilitated comparison. The glass from the case and from the window were found to give a similar bluish-purple fluorescence, but the glass from the cell gave a whitish fluorescence. Of the 22 other pieces of glass similarly examined, 4 had much the same appearance as the glass from the case and the window, whilst 18 were different. Only 1 of these 22 was similar to the glass from the case and the window in both refractive index and fluorescence.

The simplest and most discriminating test applied to the samples was that depending upon their specific gravities. Bromoform, in a stoppered glass cylinder, was diluted with benzene (the mixture being finally adjusted with half drops of benzene or bromoform), until a splinter of glass from the case remained suspended in the liquid. A few similar splinters from the glass from the window were added, and these behaved in an exactly similar manner. Glass from the cell was found to float in this liquid. Splinters of approximately similar size were broken from the 22 other pieces of glass and immersed in the liquid; 6 floated and 16 sank. The sample which was similar in refractive index and fluorescence to those from the case and the window was of slightly, but definitely higher, specific gravity than those. An additional 41 pieces of glass, of different kinds from various sources, were also similarly examined, and, of these, 30 floated in the test solution, and 11 sank. During the whole of the specific gravity tests, the splinters from the case and the window remained suspended in the liquid. The specific gravity of this liquid at 28° C. was 2·5234. As these latter 41 samples had specific gravities different from those of the specimens from the case and the window, it was not necessary to examine them by the other methods. By this test a large number of samples could be examined rapidly, and only those of specific gravity similar to that of the liquid would need to be examined further.

The glass from the cell thus differed in all three respects from the glass from the broken window, and probably had no connection with the crime.

Of a total of 65 samples of glass examined, only one agreed, in refractive index, appearance under ultra-violet light and specific gravity, with the glass from the broken window, and that was the glass from the attaché case. It was therefore considered highly probable that the splinters that were on the case were obtained from the window concerned. The accused was one of the three people found in the vicinity immediately after the crash (about 2 a.m.), and an article from inside the window was found shortly afterwards in a doorway nearby, which the accused was known to have passed after the crash. The Grand Jury questioned the analyst regarding the conclusiveness of the findings, and returned a true bill, but the common jury found the accused not guilty, principally on other grounds. The Judge asked, during the trial, what would be the chances of two pieces of glass, selected at random, agreeing in all three respects. Although it might be possible to calculate the theoretical probabilities, it was considered that as the effects of the ingredients, manufacture and distribution of glass could not all be traced, an estimate of the chances would not be justified. The definite evidence was, that of 65 samples from various sources examined, only one (that from the attaché case) agreed in all three respects with the glass from the broken window.

N. A. Marris

Dominion Laboratory
Wellington, New Zealand

THE DETERMINATION OF HYDROCARBONS IN ALCOHOL CONTAINING ACETONE

It has been found that the reaction between formaldehyde (or paraformaldehyde) and acetone can be used to eliminate acetone quantitatively from mixtures containing methyl or ethyl alcohol or these two together, thus simplifying the determination of the "spirit strength" of many commercial products. (Hoff and Macoun, Analyst, 1933, 58, 749–752.)

The purpose of the present note is to show that the same reaction can be used with advantage when small proportions of volatile hydrocarbons are to be determined when associated with the lower alcohols and acetone, as is the case with many grades of "denatured spirit."

For instance, the Canadian Government sanctions the duty-free sale of ethyl alcohol mixed with wood spirit and "petroleum benzine," "solvent naphtha" distilled from coal tar, or benzene. In these products the hydrocarbons range from 1·0 to 2·22 per cent. by volume, whilst the acetone content is usually from 10 to 15 grms. per litre. Control determinations on these mixtures are frequently demanded from this laboratory. The methods lately employed have been those which I published (*J. Soc. Chem. Ind.*, 1931, **50**, 242T), but the procedure here described has been found more convenient, accurate and rapid than those.

Into a 500-ml. Kjeldahl flask, measure 100 ml. of the material under examination. For each grm. of acetone present, add 1·5 grm. of paraformaldehyde, followed by 20 ml. of (*N*) sodium hydroxide solution. Connect the Kjeldahl flask with a reflux condenser not less than 60 cm. in length, and heat the mixture slowly to incipient boiling (best by use of an electric hot-plate). Next allow the reacting material to cool to room temperature, rinse the reflux condenser with a little alcohol followed by 250 to 300 ml. of water, and disconnect the reflux condenser, replacing it by a plain delivery tube (without foam-trap) and a vertical condenser for distillation, arranged so that the distillate may be collected in a graduated tube reading in 0·1 ml. intervals ("Eggertz tubes" are convenient for this purpose). Insert the lower end of the condenser (or of a straight "adapter" attached to it) as far as possible into the Eggertz tube, to avoid mechanical losses of the distillate. Allow distillation to proceed until 20 ml. have been collected in one graduated tube and a like amount in a second; the whole of the hydrocarbons (up to 5 to 6 per cent.) will then have passed over if the rate of distillation has been well regulated. For 2·5 per cent. or less of hydrocarbon, collect at the rate of 2 to 3 ml. per minute, but for higher proportions distil at 5 ml. per minute. To the contents of each graduated tube now add 15 ml. of potassium dichromate solution (one-sixth saturated), followed by 2 ml. of hydrochloric acid (sp.gr. 1·2). Insert a straight-sided closely-fitting rubber stopper into the mouth of each tube and mix the contents thoroughly by repeated inversions. When an olive-green colour has developed, add from a pipette to the contents of each tube 10 ml. of low-boiling light petroleum, keeping the end of the pipette close to the surface of the liquid into which it is being delivered. (With a little practice there is no difficulty in delivering an exact volume of this very volatile material.)

Re-insert the stoppers and again mix the contents of the tubes very thoroughly. Clamp the tubes vertically, stoppered ends downwards. With this precaution taken, it has been found that the volume of liquid will remain unchanged for months. After complete separation of the petroleum layer has occurred, read its volume in ml. This reading, minus 10, gives the percentage by volume of hydrocarbon in the sample.

The following table shows typical results obtained from mixtures of different hydrocarbons with ethyl alcohol, methyl alcohol and acetone, the latter varying in amount from 1·3 grm. to 2·4 grms. per 100 ml. of sample.

	Per cent. by volume			Per cent. by volume	
Hydrocarbon	Present	Found	Hydrocarbon	Present	Found
Petroleum benzine	1·0	1·0	Benzene	2·22	2·20
Petroleum benzine	1·0	1·05	Benzene	2·22	2·30
Petroleum benzine	1·0	0·95	Toluol	5·0	5·0
Solvent naphtha	1·0	1·0	Toluol	5·0	4·95
Solvent naphtha	1·0	1·0			

The method has application in the analysis of varnish solvents and other alcoholic mixtures containing acetone and hydrocarbons, diluted, if necessary, with alcohol so that the hydrocarbon-content does not exceed 5 per cent. by volume, and the acetone not more than 4 grms./100 ml. in the mixture.

Dr. Tingle, Chief of the Customs-Excise Laboratory, wishes it to be known that the above method will in future be considered the official one for Canadian Revenue cases.

RONALD W. HOFF

CUSTOMS-EXCISE LABORATORY
DEPARTMENT OF NATIONAL REVENUE
OTTAWA, CANADA

Official Appointments

THE Minister of Health has approved the following appointments:

RHYS PENDRILL CHARLES as a Public Analyst for the Borough of Poole, in addition to C. G. Moor, in place of William Partridge (died December, 1933) (July 17th).

FRANCIS EDWIN NEEDS as Public Analyst for the County Borough of Bristol, in place of Edward Russell (retired) (August 14th).

HENRY TURNER LEA as Public Analyst for the County Borough of Huddersfield, in place of L. Gordon Paul (resigned) (August 28th).

Notes from the Reports of Public Analysts

The Editor would be glad to receive the Annual or other Reports of Public Analysts containing matter of special interest to the Society. Notes made from such Reports would be submitted to the Publication Committee.

CITY OF GIBRALTAR

ANNUAL REPORT OF THE CITY ANALYST AND BACTERIOLOGIST FOR THE YEAR 1933

THE total number of specimens and samples of all classes examined during the year was 3764.

Three new Bye-Laws to the Public Health Ordinance, 1907, the Food and Drugs (Adulteration) Ordinance, 1931, dealing with the sale of milk, including condensed and dried milks, became operative during the year. These bye-laws are based on the English legislation for these articles.

MILK AND DAIRIES BYE-LAWS.—The object of these bye-laws is the control of the milk supply of Gibraltar, and all bye-laws of the Public Health Ordinance, 1907, dealing with this subject are revoked.

Of special interest to Gibraltar is the introduction of a new rule demanding the marking of every churn, vessel or other receptacle used for the conveyance of skimmed milk, or for containing such milk, when exposed for sale—the words "skimmed milk" or "separated milk," as the case may require, being used in large and legible type.

For many years attention has been drawn to the large proportion of imported goats' milk which is deficient in milk fat when sold to the public. For the year 1933 over 50 per cent. of the goats' milk samples were below the statutory limit of 3·5 per cent. of fat. At times as much as 40 per cent. of the fat has been found to be extracted. It is seen, therefore, that some control over the sale of this article was necessary.

Imported Unboiled Milk.—As a large proportion of Gibraltar's milk supply comes from Spain, and is thus beyond the control of the City Council, the only safe protection against the introduction of milk-borne diseases (enteric, undulant fever, etc.) is by boiling the milk before vending. This is a wise and necessary precaution. The offering, or exposing for sale, of unboiled imported milk is a serious offence, and one with which the magistrates deal severely. Among last year's samples three (cows' 2, goats' 1) milks were found not to have been boiled, pasteurised, or sterilised. Three other samples showed evidence of the presence of some unboiled milk, amounting to approximately two per cent.

Food Poisoning by Lobster.—Numerous cases (over 80) of food poisoning, with the usual symptoms of vomiting, diarrhoea, and gastric pains, occurred on a passenger ship visiting Gibraltar. No evidence of mineral poisons could be found, and micro-organisms of the food-poisoning group could not be isolated from any of the materials submitted (gastric contents, faeces, water, and boiled lobsters). Feeding experiments with the lobsters, however, caused severe vomiting and diarrhoea, and the explanation of the outbreak is that at one time the lobsters harboured micro-organisms of the Salmonella group, which were killed when the lobsters were boiled, whilst their toxins, being thermo-stable, were not destroyed.

Tests for Sea Water in Natural Waters.—In an investigation of the natural waters occurring at the north end of the Colony many borings at different depths were made, and over 100 samples were submitted for analysis. Samples of water from borings a few feet deep contained chlorine in normal amounts while samples from the same borings, obtained after passing impermeable strata at about twenty feet, contained chlorine in excessive quantities. In another instance water, appearing to percolate direct from the "Rock," contained much chlorine. From the figures of mineral analyses of six specially selected waters containing excess of chlorine a firm of analytical chemists in London concluded that the presence of sea water was the cause of the high chlorine content in all six samples. They based their conclusions on the ratio of magnesium to sodium found in the samples. The ratio was constant and agreed closely with that found in pure sea water. I was able to show also that other ratios occur which are also significant and confirm the conclusions arrived at in London. In one instance only 3 per cent. of sea water was calculated to be present, yet the three ratios referred to held good for sea-water contamination. Entirely different ratios were obtained when examining waters which percolate from the "Rock" far too high above the sea to allow of sea-water contamination. In one of these, although chlorine and sulphates were prevalent (as in sea water), there was no indication, when comparing ratios, that sea water was present.

Points observed were:—

Water containing sea water.	*"Rock" water not containing sea water.*
(1) Magnesia exceeds lime approx. 2 to 1.	Lime exceeds magnesia approx. 3 to 1.
(2) Chlorides exceed sulphates by approx. 8 to 1 (constant).	Chlorides exceed sulphates by only 3 to 1.
(3) Sodium exceeds magnesium by approx. 4·5 to 1 (constant).	Sodium exceeds magnesium by only 2 to 1.

A. G. Holborow

Legal Notes

Under this heading will be published notes on cases in which points of special legal or chemical interest arise. The Editor would be glad to receive particulars of such cases.

ALLEGED ADULTERATION OF MILK WITH WATER. THE HORTVET TEST

AT the Hull City Police Court on July 27th, 1934, before the Stipendiary Magistrate, a tradesman was summoned for selling, on two occasions, milk which was alleged to have been adulterated with water. There were four summonses, and the respective amounts of added water were alleged to be 4·5, 5·7, 5·8 and 5·7 per cent. Mr. J. Boyle, Assistant Solicitor to the Corporation, prosecuted, and Mr. B. Pearlman defended.

Mr. Boyle said that at a previous hearing the defendant, through his solicitor, applied for the reserved portions of the four samples to be sent to the Government Chemist for analysis. That was about seven weeks after the samples were taken, and naturally the milks were in a sour condition. The Government Chemist had analysed the milks, and his certificates showed results somewhat different from those of the City Analyst, who analysed the milk samples when fresh and also carried out the Hortvet method for the determination of the freezing-point. This method could not yet usefully be applied to sour milk. Mr. Boyle further said that the differences in the analyses were merely working differences between two analysts, when working on fresh and sour milk respectively. The Government Chemist's certificates were as follows:—

Milk No.	1 Per Cent.	2 Per Cent.	3 Per Cent.	4 Per Cent.
Fat	2·81	2·98	3·04	3·19
Non-fatty solids*	8·65	8·56	8·54	8·50
Ash	0·69	0·71	0·71	0·70
(Loss on keeping	0·16	0·15	0·16	0·18)

* After corrections for loss on keeping.

Opinions based on these results and the Sale of Milk Regulations, 1901, were added.

The City Analyst (Mr. A. R. Tankard, F.I.C.) said that he obtained the following results on analysis of the four samples:—(i) Non-fatty solids, 8·44 per cent.; fat, 2·93 per cent.; freezing-point (Hortvet), —0·506° C.; (ii) 8·44 per cent. and 3·06 per cent.; freezing-point (Hortvet), —0·500° C.; (iii) 8·41 per cent. and 3·10 per cent.; freezing-point (Hortvet), —0·499° C.; (iv) 8·40 per cent. and 3·21 per cent.; freezing-point (Hortvet), —0·500° C. The amounts of added water indicated from the freezing-points were those already stated, —0·530° C. being taken as the upper limit for genuine milk. Mr. Tankard maintained that by the determination of the freezing-point definite proof of the presence of added water was obtained in the cases where the depression was less than —0·530° C. He was satisfied with the method in this case as carried out in his laboratory, and had proved that his results obtained by the Hortvet procedure agreed very closely with those obtained in other laboratories. The freezing-point test distinguished between milk which was naturally poor and that which contained extraneous water. If defendant sold, as stated, 20 gallons of milk daily, seven pints of water were sold as milk each day. There was nothing in the certificates of the Government Chemist which was inconsistent with the presence of water in these samples.

Mr. A. More, A.R.C.Sc., F.I.C., Superintendent Chemist in the Government Laboratory, giving evidence on subpoena, said that the figures in the certificates of the Government Chemist were in fair agreement with those of the City Analyst. It was, of course, easier to get accurate results when analysing fresh milk than when dealing with very sour milk. On the average, it was found that the fat, as determined on the sour milk, was about 0·1 per cent. less, and the non-fatty solids (including corrections calculated from the various products of decomposition) 0·1 per cent. more, than the figures found on analysis of the fresh portion of milk, but in certain instances the differences were somewhat larger. He agreed with the statement that the Hortvet technique was a valuable method for the detection and determination of added water in milk, and assuming the figures given by the City Analyst, he said that they all pointed to the presence of water in these samples. He agreed with the limit of —0·530° C. as the smallest depression of the freezing-point compatible with the genuineness of milk, when ascertained by the Hortvet technique. The presence of 8·5 per cent. of non-fatty solids in milk was no guarantee of the absence of extraneous water in such milk. Where, in the certificates of the Government Chemist, it was stated that "it can not be presumed that the sample is not genuine," that statement was in relation to the presumptive standard of the Sale of Milk Regulations.

Mr. G. D. Elsdon, B.Sc., F.I.C., County Analyst for Lancashire, gave evidence of his pioneer work in this country in connection with the Hortvet method, and stated that he had 1200 or more results which confirmed him in the opinion that genuine milk showed a freezing-point depression (Hortvet) of not less than —0·53° C. He stated that this method was of the greatest value in determining the purity of milk in relation to added water, and that on the figures obtained by the City Analyst there was conclusive evidence of added water in all the four samples, to the minimum extent given in Mr. Tankard's certificates.

For the defence, Mr. Pearlman called Mr. J. A. Foster, F.I.C., County Analyst for the East Riding of Yorkshire, etc., who said that in three of the four samples of milk in question there was a surplus of fat. The Hortvet method of analysis was useless after two or three days had elapsed. Mr. H. Thompson, also called for the defence, stated that he analysed the samples when three weeks old, and found results for fat and non-fatty solids differing from those of the City Analyst only in the second place of decimals. He did not do the Hortvet test.

The defendant and his milk salesman gave evidence that they had not tampered with the milk, which came from three sources and was mixed milk. Mr. Pearlman said that when they knew the results of Mr. Tankard's analyses it was too late to do anything, so far as the Hortvet test was concerned. He asked the Magistrate to believe his client when he said that he never extracted fat or added water to the milk, and to say that he did not accept the infallibility of the Hortvet or any other process. The defence could not challenge Mr. Tankard or anyone else, because it was too late when the summonses were issued.

Dealing with the Hortvet method, the Stipendiary Magistrate said that if the method was all that Mr. Tankard claimed it to be, it was an extraordinarily useful thing. The defence had only to prove an instance in which the method had failed, and he would have rejected it without hesitation. As they had not done so, he accepted the Hortvet process. He accordingly decided that the samples contained added water. In convicting the defendant, he inflicted fines of £1 on one summons and 5s. on each of the other three, with two guineas costs in each case, a total of £10 3s. 0d.

"LIQUID CHOCOLATE" DEVOID OF CHOCOLATE

On July 21st a Mitcham firm of manufacturers was summoned at Aylesbury Petty Sessions for having issued a false label with an article of food sold by them, and for giving a false warranty under the Food and Drugs Act.

Mr. T. H. Jenks, prosecuting for the Buckinghamshire County Council, said that the first charge was that of giving with an article of food, known as "choc" chocolate, a label which falsely described the article. "Choc" chocolate was sold to confectioners for the purpose of making articles of chocolate confectionery, but, when analysed, it was found to contain no chocolate. A sample was taken from a tin supplied to an Aylesbury confectioner, who had bought it under the impression that he was buying liquid chocolate. The article was invoiced as "liquid choc," and he had purchased it under a warranty given by the manufacturers that the article was pure and complied with the requirements of the Food and Drugs Act.

Mr. Eric Voelcker, F.I.C. (Public Analyst for Buckinghamshire), said that he had found the contents of the tin to consist mainly of an artificial brown dyestuff. The label on the tin was misleading, because the article contained no chocolate.

The defendants pleaded guilty, and their works manager explained that they had been making "choc" for 13 or 14 years. Until three years ago all their labels bore the words "Choc colour of strength," but in 1931 their labels were revised, and, with no intention of misleading anyone, the words "Choc chocolate" were used. He produced a leaflet describing it as "Liquid choc-true chocolate colour of undoubted merit." It was always known to the trade as "liquid choc." Since the proceedings all labels had been withdrawn.

In reply to Mr. Jenks, he said that the use of the word "chocolate" was a technical error.

A fine of £5 on each charge, with 12 guineas special costs, was imposed.

MERCHANDISE MARKS ACT

Lysol Prosecutions

At Salford City Police Court, on August 15th, a number of summonses were heard in connection with the alleged contravention of section 2 (1 & 2) of the Merchandise Marks Act, 1887. The retailer was charged with the sale of an article to which a false trade description had been applied, and the manufacturers and wholesalers were charged with aiding, abetting, counselling and procuring the retailer in the commission of the offence. The manufacturers were also charged with unlawfully applying a false trade description, namely, Lysol, to a solution of cresols containing 2·4 per cent. of cresol and labelled "Dr. Kohl's British Made Lysol Solution, contains under 3 per cent. cresols."

Mr. J. H. Smith, Deputy Town Clerk, prosecuting on behalf of the Salford Corporation, submitted that the public bought such articles believing them to be Lysol, and that the sale was therefore a fraud which might in certain circumstances be a dangerous fraud. Inspector Stott described the purchase; he asked for Lysol, and was supplied with the bottle in the carton which he produced. Each was labelled "Dr. Kohl's British Made Lysol Solution, containing under 3 per cent. of cresols".

The City Analyst, Mr. H. E. Monk, said that the sample contained cresol, 2·4; caustic alkali, 0·9; water, 96·7 per cent. According to the British Pharmacopoeia definition of Lysol the sample was 94·9 per cent. deficient of the minimum amount of cresol and totally devoid of soap. An approximately similar solution could be made by diluting 5 parts of Lysol with 95 parts of water. While, in his view, in the absence of soap, the sample could not even be called diluted Lysol, the most serious thing was not shortage of soap, but shortage of cresol. He did not agree that the words "Lysol solution" on the label would be understood by any purchaser to mean a dilution of Lysol; Lysol was itself a solution, and was so described in the Pharmacopoeia. He would not agree that there were many differing standards for Lysol. Differences were possible in the kind and amount of soap used to render the cresol soluble, but the percentage of cresol must be 50 per cent. The statement "contains under 3 per cent. of cresols" was perfectly intelligible to him, but would not be understood by the ordinary purchaser.

Mr. E. H. Simmons, a registered pharmacist and a member of the Council of the Pharmaceutical Society, said that he remembered the introduction of Lysol into this country. At that time it had contained 50 per cent. of cresols, and it had contained 50 per cent. of cresols ever since. It was understood in his trade that Lysol meant 50 per cent. of cresols. He certainly would not sell such an article as the sample in answer to a demand for Lysol. Its use, under the impression that it was Lysol, might well have serious results.

Dr. G. J. Crawford, City Pathologist and Bacteriologist, said that the phenol-coefficient was 1/60. Using the dilution recommended upon the label for wounds, he found that organisms were not killed in half an hour, but by using the dilution (1 per cent.) recommended upon a bottle of genuine Lysol the organisms were killed by the latter in 2½ minutes. To use this article as a disinfectant might be worse than using none at all; its use would give a false feeling of security.

Mr. Kenneth Chambers, Barrister, for the defence, contended that they were protected by the word "Solution," which, with the statement as to cresol-content, clearly showed the article to be a diluted Lysol. There was no intent to defraud.

In giving his decision the Stipendiary Magistrate, Mr. Percy Macbeth, said that he had power to fix a standard. He held that Lysol must contain 47 to 53 per cent. of cresols, and that the use of the word Lysol upon the label and carton amounted to a false trade description. He thought that the wholesaler and retailer knew very little about it; he would fine the retailer 5s. and the wholesaler 20s. The makers would be fined £10 for applying a false trade description, and £2 for aiding, abetting, counselling and procuring the sale, with eight guineas costs.

Similar fines were imposed in the case of "Dr. Emrad's British Made Lysol." The facts were similar to those in the preceding case, except that the word "solution" and the declaration as to cresol-content appeared only on the bottle and not upon the outer carton. The article itself contained soap, and was, in fact, a five per cent. dilution of Lysol.

Ministry of Agriculture and Fisheries

SPECIFICATIONS AND METHODS OF ANALYSIS OF CERTAIN INSECTICIDES AND FUNGICIDES*

As a result of discussions between representatives of the National Farmers' Union, the insecticide and fungicide makers and the Ministry, the Association of British Insecticide Manufacturers undertook to bring up to date the specifications published in Advisory Leaflet No. 9, and to add specifications for certain compounds not previously dealt with: these latter include copper fungicides for potato-spraying, which had been specially mentioned by growers' representatives as having caused difficulty. The Association has now prepared these specifications, which have been accepted by the Government Chemist, the National Farmers' Union, and the Ministry, and which are printed below; in addition, and no less important, agreed methods of analysis have been drawn up in connection with the specifications, for the use of analytical chemists.

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* Bull. No. 82, pp. 12, July, 1934. H.M. Stationery Office, Adastral House, Kingsway, W.C.2. Price 3d. net.

Members of the Association of British Insecticide Manufacturers, and certain other firms, have agreed to conform to these standards, and purchasers of the insecticides and fungicides in question are strongly advised to require a guarantee that materials supplied shall comply with these specifications. By so doing, they will make certain of obtaining standard products of high quality.

SPECIFICATIONS FOR CERTAIN STANDARD PRODUCTS

(1) **Lead Arsenate.**—The specifications given apply to the form diplumbic arsenate ($PbHAsO_4$). (*a*) *Powder* must contain not less than 31 per cent. of arsenic (as As_2O_5), not less than 63 per cent. of lead oxide (PbO) and not more than 0·5 per cent. of water-soluble arsenic as As_2O_5. (Manufacturers of lead arsenate powder containing spreaders or wetting agents should declare the amounts of the abovementioned constituents.) It shall conform to the limit test for acidity.

(*b*) *Lead Arsenate Paste.*—Must be of uniform consistence, form a fine cream when rubbed with water, and consist essentially of $PbHAsO_4$ (diplumbic arsenate). It shall contain not less than 14 per cent. of arsenic (as As_2O_5), not less than 28·4 per cent. of lead oxide (PbO); not more than 0·5 per cent. of water-soluble arsenic (as As_2O_5) calculated on the dry basis; and shall conform to the limit test for acidity.

(2) **Lime-Sulphur Solution.**—Shall be clear and free from sludge; sp.gr. approximately 1·3; shall contain not less than 18·5 per cent. by weight of polysulphide sulphur.

(3) **Nicotine and Nicotine Sulphate.**—The manufacturer shall declare the content of nicotine and that it is substantially free from coal-tar base.

> *Note.*—The term "Nicotine" is generally understood to mean a pure or commercially pure product of 95 to 98 per cent. strength; it is often loosely employed by some sellers to designate nicotine sulphate containing 40 per cent. of nicotine or materials containing between 40 and 95 per cent. of nicotine.

(4) **Copper Sulphate.**—Shall contain not less than 98 per cent. of $CuSO_4, 5H_2O$.

(5) **Bordeaux Powder.***—This is composed of copper sulphate and lime (calcium oxide or hydroxide). The equivalent content of copper (Cu) shall be declared. No water-soluble copper to be present.

(6) **Burgundy Powder.***—Burgundy powder is a mixture of copper sulphate and sodium carbonate. The equivalent content of copper (Cu) should be declared. Alkalinity (as Na_2CO_3) not to exceed 2 per cent. No water-soluble copper to be present. The whole of the powder shall pass through a 30-mesh British Standards sieve (B.S.S. 410, 1931).

(7) **Cheshunt Compound.**—This is a mixture of 2 parts by weight of copper sulphate and 11 parts by weight of ammonium carbonate, as defined by the Cheshunt Research Station. It shall contain not less than 3·8 per cent. of copper (Cu).

(8) **Soft Soaps for Spraying Purposes.***—When tested by the prescribed methods, soft soap for spraying purposes shall conform to the following requirements:—

(1) It shall dissolve completely in distilled water to a clear solution.

(2) It shall contain not more than 1 per cent. of free caustic alkali, calculated as potassium hydroxide (KOH) and not more than 3 per cent. of free alkali carbonate, calculated as potassium carbonate (K_2CO_3).

(3) Not less than 95 per cent. of the total alkali expressed as potash (K_2O) shall be potash (K_2O).

(4) The percentages of fatty and of resin acids shall each be declared.

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* At present a specification affording a complete guide to efficiency cannot be prepared. The purchaser is advised to obtain only the products of reputable British manufacturers.

(9) **Cyanides.**—(*a*) *Sodium Cyanide.*—Sodium cyanide shall contain not less than 97 per cent. of sodium cyanide.

Note.—The strength of sodium cyanide is frequently expressed in terms of potassium cyanide. Since 100 parts of pure sodium cyanide are equivalent, as regards hydrocyanic acid content, to 132·8 parts of potassium cyanide, sodium cyanide of 97–98 per cent. strength is often spoken of as "129–130 per cent. cyanide."

(*b*) *Potassium Cyanide.*—Potassium cyanide shall contain not less than 93 per cent. of potassium cyanide.

(*c*) *Calcium Cyanide.*—Calcium cyanide shall contain not less than 40 per cent. of calcium cyanide.

(10) **Formaldehyde.**—Commercial formaldehyde (formalin) is essentially a colourless solution of formaldehyde in water, neutral or faintly acid to litmus. It shall contain not less than 36 and not more than 40 per cent., weight in volume, of formaldehyde (H.CHO), when tested by the prescribed method.

PRESCRIBED METHODS OF ANALYSIS

SPECIAL NOTE.—It is ***most important*** that the methods of analysis prescribed shall be read in conjunction with the specifications to which they refer.

The greatest care must be exercised in taking samples for any purpose. They must be truly representative of the bulk of the material, otherwise misleading results will be obtained.

The methods, which are described in detail, occupy six pages, and are grouped under headings corresponding with the various classes of products included in the specifications. For the determination of polysulphide sulphur the method of Goodwin and Martin (*J. Agric. Sci.*, 1925, **15**, 96; Abst., ANALYST, 1925, **50**, 148) is recommended. The methods for the determination of nicotine are modifications of Bertrand's silicotungstic acid precipitation method (*Bull. Soc. Chim.*, 1899, **21**, 434; Abst., ANALYST, 1899, **24**, 187).

The methods prescribed for the determination of the cyanide-content of sodium, potassium, and calcium cyanides are those given in the A.O.A.C. *Methods of Analysis*, 3rd Ed., 1930, p. 51, 52.

Department of Scientific and Industrial Research

REPORT OF THE FOOD INVESTIGATION BOARD FOR 1933*

THE Annual Report of the Food Investigation Board for the year 1933 reviews the aims of the research work, now costing about £45,000 a year, carried out by the Department on the transport and storage of foodstuffs. These aims, the Report states, have not always been fully understood. The object of the work is, and always has been, the improvement of the food-supply for the people of this country.

The General Report of the Board (pp. 1–16) is followed by the Director's Report, which comprises an Introduction, and accounts of the work done at the Low Temperature Research Station (pp. 19–164), The Torry Research Station (pp. 167–190), and the Ditton Laboratory (pp. 193–211), and of the Extra-Mural work (pp. 212–230), which includes researches conducted at the National Physical Laboratory, and at the Imperial College of Science and Technology.

SECTION A. MEAT.—Investigations on the physiology of muscle protein, on the evaporation of water from tissues, and on the freezing of tissues (*cf.* ANALYST, 1933, **58**, 611) have been continued, and the results have been published (references given). A new method has been devised for determining the amount of ice in muscle at different temperatures.

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* H.M. Stationery Office, Adastral House, Kingsway, W.C.2. Pp. 248. Price 4s. net.

The Freezing of Eggs.—In contradistinction to the equilibrium between yolk and white in fresh eggs, it has been found that after slight freezing and thawing the freezing-points of yolk and white rapidly move towards the same value. Eggs have been frozen at —1°, —3°, and —5° C. with the same result; there is no evidence of a critical temperature of freezing, as found with living muscle.

The Colour of Beef-fat.—The chief factors which determine the appearance of the external adipose tissue of a carcase of beef are, (i) the concentration of the yellow carotinoid pigment in the fat, (ii) the quantity of haemoglobin present, and (iii) the optical properties of the superficial layer of connective tissue and the fat immediately beneath it. There is usually a marked variation in appearance at different points on the surface.

From further experiments on the effect of carbon dioxide on the colour of beef-fat the conclusion has been drawn that the addition of 10 per cent. of carbon dioxide to the air does not increase, to any significant extent, the rate of oxidation of the haemoglobin present in the fat. With high concentrations of carbon dioxide the rate is markedly increased.

Aldehydes in Rancid Fats.—The bisulphite method of determining aldehydes in rancid fats has been investigated, and the results have been published (*Ind. Eng. Chem., Anal. Ed.*, 1934, **6**, 241; see Abst., p. 702). Preliminary experiments have indicated that zero values are obtained with perfectly fresh samples of fat.

Minimum Temperatures of Growth of Bacteria.—The further results obtained indicate that bacteria of the *Achromobacter* and *Pseudomonas* groups are capable of growth on frozen meat and potatoes down to at least —3° C. Those bacteria having optimum temperatures for growth at 37° C. cease growth, or grow very slowly, in the range +5° to 0° C., notably *Staphylococcus aureus*, *B. coli communis*, etc. On the other hand, such organisms as have optimum temperatures for growth around 20° C. usually grow well at 0° C., most strains of *Pseudomonas* and *Achromobacter* growing slowly at —3° C., but not below. One strain of *Pseudomonas*, however, grew at —5° C. in ten weeks on supercooled agar. Up to about 90 per cent. of the individual bacteria comprising the pure strain are capable of growth down to —3° C., but in the single case of growth so far obtained at —5° C., the viable percentage had fallen to about 70 per cent.

Preliminary work suggested that when whole carcases are hung in cold stores at 0° C., with still, unconditioned air-supply of relative humidity varying from 70 to 80 per cent., little, if any, multiplication of the bacteria present takes place on the fatty or connective tissue.

Effect of Ozone on the Growth of Bacteria.—Preliminary experiments indicate that organisms vary in their resistance to ozone, *Staphylococci* and *Proteus* being more resistant than *Achromobacter*.

The germicidal concentration towards *Achromobacter* of ozone, introduced at the same time as the inoculation, appears to be about 300 parts per million by volume at 20° C. and 10 to 100 parts per million by volume at 0° C. Ten parts per million had some inhibitory effect on certain bacteria at 0° C.

Storage of Meats in Carbon Dioxide.—The maximum permissible concentration of 20 per cent. of carbon dioxide in the atmosphere is dictated by considerations of bloom. If it is desired to store the meat in higher concentrations of carbon dioxide, it is necessary to increase the proportion of oxygen, since otherwise the colour or bloom of the meat rapidly disappears, owing to the formation of methaemoglobin.

The respiration of dead muscle is between 10 and 50 per cent. of that of living muscle, the amount depending upon the method of killing and on the *post-mortem* history. Carbon dioxide can be absorbed by meat by solution in both muscle and fat, and, to a slight extent, by conversion into bicarbonate ion.

If any benefit is derived from inflating carcases with carbon dioxide, it is probably due to the introduction of sterile gas rather than the ordinary infected air of the slaughter-house.

The storage of meat has been made the subject of a special report (No. 43, *cf.* ANALYST, 1934, 175).

SECTION B. FRUIT AND VEGETABLES.—It was reported last year (*loc. cit.*) that ripe apples give off some substance which, even when present in the air in very small quantities, stimulates the irreversible change, termed the climacteric, which ushers in the senescent phase of life, and which is accompanied by a marked increase in respiratory activity. It has now been shown that bananas, peaches and pears, but not oranges and grapes, also produce this or a similar substance.

The fact that post-climacteric apples evolve a substance which induces the climateric in other apples which have not yet reached the stage at which it is auto-induced, has the interesting result that when apples are kept confined together in a group, the climacteric occurs nearly simultaneously in all the individuals at about the time when it is auto-induced in the most advanced fruit of the group; while if similar apples are isolated in separate containers, the self-induced climacterics are spread over a considerable interval.

The postponement of the climacteric, and of the concomitant increase in respiratory activity, is accompanied by a corresponding lengthening of the life of the fruit. It has now been shown that the effect of carbon dioxide in the atmosphere, as in gas-storage, is not only to depress post-climacteric respiratory activity, but also to delay markedly the occurrence of the climacteric itself. In the analysis of the factors affecting the climacteric, it has been found that supernormal concentrations of oxygen in the atmosphere accelerate the occurrence of the climacteric, whilst subnormal concentrations delay it. Ozone in concentrations of about 50 parts per million appears to induce its immediate occurrence. In the absence of oxygen, the irreversible climacteric rise in respiratory activity is not induced by ethylene, as it is in air, nor is there any latent stimulus, for on return to air after such treatment the apples are still pre-climacteric. Oxygen is therefore definitely concerned in the mechanism by which ethylene stimulates the onset of the climacteric. Last year, it was suggested, by analogy, that ethylene might be the active substance evolved by ripe fruit. It has now been found that, whereas ethylene does not induce the occurrence of the climacteric in the absence of oxygen, nevertheless the climacteric can be auto-induced in such conditions.

The total volatile products of the metabolism of fruit, other than carbon dioxide, are now being measured, and it has been found that their production increases at the climacteric, and that a large part of them can be retained by phosphorus pentoxide or concentrated sulphuric acid.

Another important fact established during the year is that, with the progress of senescence of apples in air, there is a steady rise in the amount of alcohol and acetaldehyde present in the flesh. It will be recalled that the tentative conclusion has been drawn from work already reported that acetaldehyde is a critical intermediate product in the breakdown of sugar, and that the fate of the sugar, either as alcohol and carbon dioxide (fermentative end-products) or as carbon dioxide and water (oxidative end-products) depends upon the concentration of acetaldehyde in the tissues. It is now further suggested that senescence in air is characterised by a progressive failure in the mechanism for the oxidative removal of acetaldehyde, and, moreover, that this failure is due to a toxic action of oxygen.

CANNING.—The variation of the steel base of tin-plate has been further studied, but cannot yet be related to the method of manufacture. Incidentally, it has been found that hydrogen can penetrate through steel and tin-plate, and form blisters on the side of the sheet opposite to that actually in contact with the corroding medium.

Metals, such as stainless steel, copper, and various alloys containing copper which are used in the manufacture of equipment for the food industry, have been further investigated, and the breakdown of a sample of stainless steel under air-free conditions, and the methods by which it was again rendered passive, are of interest.

The rate of destruction of pectin by enzymes, as indicated by the strength of the pectin-sugar-acid gel prepared from fruits stored for six to eight months at temperatures of —10° C. and —20° C., is being determined. No measurable destruction has been found at the lower temperature, but at the higher it was between 15 and 25 per cent. with raspberries, and 35 per cent. with gooseberries.

The effect of various methods of canning on the vitamin in apples has been considered, in collaboration with the Medical Research Council. It has been confirmed that soaking in weak brine before canning protects vitamin *C*, and that leaving the peel on unsoaked slices has a similar effect. The canned peel of Bramley's Seedling apples is particularly rich in vitamin *C*.

FISH.—At the Torry Research Station the study of the effects of cold storage on the flesh of fish has been continued. The production of "drip" in relation to temperature and length of storage, differences in response to cold storage of different species of fish, and the behaviour of thawed-out, brine-frozen fish in comparison with fresh fish when packed in ice, are topics that are under consideration.

In continuation of the work on the metabolism of fat in fish, data obtained support the theory that the high selectivity of the animal in laying down its depôt fats, rests on the basis of filtration by molecular size.

Vitamin A in Halibut-liver Oil.—The large fluctuations in the amounts of vitamin *A* found in the halibut's liver appear to be seasonal, and to be related to the fluctuations in the numbers of diatoms in the sea.

Bacteria in Fish.—Marked differences are found in the inhibitory effect of carbon dioxide on the growth of certain bacteria isolated from fish. Thus, an *Achromobacter* of the type constantly present in the slime of fresh fish is extremely sensitive, while *Aerobacter cloacae*, an organism found on stale fish, is but little affected. It is suggested that a change in the acidity of the medium, resulting from incubation in carbon dioxide, is largely responsible for the inhibition of the *Achromobacter's* growth.

Glycogen and Lactic Acid.—The breakdown of glycogen and the accumulation of lactic acid in fish's muscle are affected by actually freezing the muscle, and in that state the maximum rate of change occurs within the range of temperature —2·5° to —3·5° C. A closer determination is aimed at. The existence of a seasonal variation, related to spawning, in the glycogen of fish's muscle is a further point of interest which has been brought out by these experiments.

Draft Poisons List and Rules

UNDER Part II of the Pharmacy and Poisons Act, 1933 (*cf.* ANALYST, 1933, 58, 548), an Advisory Committee known as the Poisons Board was constituted in November, 1933 (ANALYST, 1934, 43), for the purpose of preparing a list of the substances to be treated as poisons for the purposes of the Act. The Poisons Board has now prepared a draft list of poisons and draft rules for circulation to the interests likely to be affected by them. The list and the Rules are not necessarily in the form in which they will be submitted by the Poisons Board to the Home Secretary, who has power under the Act to vary the recommendation of the Board. It is open to any interested body to make any representations to the Poisons Board upon any matters contained in the drafts.

The List consists of two parts. Part I comprises those poisons which can be sold only by "authorised sellers of poisons," whilst poisons under Part II may also be sold by persons whose names appear on a local authority's list. There is also a list of Exclusions, containing substances which are not to be treated as poisons for the purposes of the Pharmacy and Poisons Act, 1933.

The Draft Poison Rules are given under the following seven headings:—Part I, dealing with the interpretation of the Rules; Part II, dealing with labelling and containers; Part III, with prohibitions and restrictions; Part IV, with restrictions in regard to the retail sale of poisons; Part V, storage and transport; Part VI, miscellaneous; and Part VII, giving provisions relating to the extent of the application of the Act and of these rules.

There are seven schedules:—I, Poisons to which special restrictions apply. II, Articles requiring to be labelled with a prescribed indication of character and the indication of character prescribed. III, Form of certificate for the purchase of a poison. IV, Form of entry to be made in the book to be kept by the sellers of poisons. V, Substances not to be transported in the same vehicle as food. VI, Form of application to be made to the Local Authority by a person desiring to have his name entered on the list kept by local authorities. VII, Forms of the list to be kept by local authorities in pursuance of Section 21 of the Act.

The draft Rules contain no special provision controlling the sale or supply of barbituric acid derivatives, phenyl-cinchoninic derivatives (Agotan, Atophan, etc.), and the nitrophenols (Dekrysil, etc.), which are to be made the subject of separate regulations.

The Secretary of the Poisons Board is Mr. M. D. Perrins, of the Home Office, to whom any communications to the Board should be addressed.

Clove Produce Control*

ORDINANCES have been passed by the Legislative Council in Zanzibar establishing a new and stronger Clove Growers' Association, penalising the adulteration, and regulating the marketing and export of cloves. The transfer or assignment of a clove exporter's licence is prohibited, and, if necessary, the British Resident has power to restrict the number of licences. Power is given to any member of the Licensing Authority to inspect the premises of exporters and the cloves stored therein, and to call for and examine the books.

The Clove Export Rules, which come into force on October 1st, 1934, include (Rule 6) specifications of the grades of cloves for export, as follows :

Grade I.—Good sound cloves which are whole, bright, bold and uniform in size, free from koko† and mustiness, and which contain not more than 3 per cent. of stems and extraneous matter and 16 per cent. of moisture.

Grade II.—Good sound cloves which are bold but somewhat irregular in size and free from mustiness and which contain not more than 3 per cent. of stems and extraneous matter, 5 per cent. of koko, 16 per cent. of moisture.

Grade III.—Cloves which are irregular in size and which contain not more than 5 per cent. of stems and extraneous matter, 15 per cent. of koko, 16 per cent. of moisture.

A consignment shall not be passed for export if any bale or package in that consignment fails to satisfy the standard prescribed for Grade III cloves, or be passed for export as of any special grade if any bale or package in the consignment fails to satisfy the standard prescribed in Rule 6 for that grade. The three stamps for the grades are Z1, Z2, Z3, each in a circle (*cf.* ANALYST, 1934, 628).

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* *Perfumery and Essential Oil Rec.*, 1934, 25, 239.

† The native word for immature cloves.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs Analysis

Mineral Constituents and Freezing-point of the White and Yolk of Hens' Eggs. J. Straub and C. M. Donck. (*Chem. Weekblad*, 1934, **31**, 461–465.)—Analyses of the ash of the white and yolk of hens' eggs, respectively, are as follows (in mgrms. per 100 grms. of material), and are in agreement with those found by Iljin (*cf.* J. Needham, *Chemical Embryology*, 1931, Vol. I, p. 302):—Potassium, 144·0, 117·4; sodium, 142·0, 51·7; calcium, 13·8, 151·3; magnesium, 15·9, 22·3; chlorine, 156·2, 178·0; phosphoric acid (HPO_4''), 32·45, —; carbonic acid (HCO_3'), 201·1, —; dihydrogen phosphate (H_2PO_4'), —, 1787·7; the dextrose-contents were 500 and 250, respectively. Three ignitions were required, *viz.* (i) with lime to give chlorine, potassium and sodium (by the uranyl acetate method); (ii) with sodium hydroxide, for calcium and magnesium and check determinations of chlorine and of phosphate (by the basic iron phosphate method, *cf.* Bougalt and Cattelain, *J. Pharm. Chim.*, 1931, **14**, 97); and (iii) with sodium hydroxide and sodium nitrate for the phosphates. The concentrations of the above ions in 100 grms. of water, and thence the corresponding depressions of freezing-point, were calculated; for egg-white the value of the sum of these (0·435° C.) agrees well with the experimental value, indicating that the inorganic components occur chiefly in the water-phase. The fact that the osmotically-active cations exceed the anions by 3·99 milli-equivalents per 100 grms. of water in this case is attributed to the proteins present, and an attempt is made to compensate for these. With the yolk, the difference between the observed and calculated depressions is greater, and this is due to the presence of a large portion of the calcium and phosphorus in the un-ionised form (*e.g.* as in lecithin). An attempt is thence made to deduce the respective compositions of protein-free artificial sera which would be in membrane-equilibrium with the white and yolk. J. G.

Carbohydrate-content of the Proteins in the White of Hens' Eggs. M. Sørensen. (*Compt. rend. Lab. Carlsberg*, 1934, **20**, No. 3, 1–19.)—The orcinol method of M. Sørensen and Haugaard (Abst., ANALYST, 1933, **58**, 492) has been applied to the determination of the nature and amount of the true carbohydrates in the various proteins in the white of hens' eggs. Five fractions were studied:—(i) Globulin was separated (with mucin, *vide infra*) by adding to the beaten and sieved whites an equal volume of a saturated solution of ammonium sulphate; it constitutes about 7 per cent. of the total protein and contains 4 per cent. of mannose. (ii) Mucin, which was obtained by further fractional precipitation of the globulin fraction with ammonium sulphate, constitutes about 2 per cent. of the total protein and contains 14·9 per cent. of a mixture of equal quantities of mannose and galactose. (iii) Albumin (obtained by crystallisation from the filtrate after removal of the globulin and mucin) constitutes about 70 per cent. of the total protein, and contains 1·7 per cent. of mannose. (iv) Conalbumin was precipitated by stirring the filtrate from fractions 1 and 2 with a mixture of equal volumes of solutions of N acetic acid, N sodium acetate, and saturated potassium-sodium sulphate, followed by heating on the water-bath for 20 minutes (9 per cent. of the total protein, and containing 2·8 per cent. of a mixture of 3 parts of mannose and 1 of galactose). (v) The mucoid fraction, precipitated by alcohol from the filtrate from the conalbumin fraction, constitutes about 13 per cent. of the total protein and contains 9·2 per cent. of a mixture of 3 parts of mannose and 1 of galactose. The raw white of egg also contains 0·45 per cent. of free glucose. The possibility is discussed that these carbohydrates are present in the form of polysaccharides containing three trisaccharides composed of 2 molecules of mannose and 1 of glucosamine, and one trisaccharide composed of 2 molecules of galactose and 1 of glucosamine. The results are in agreement with S. P. L. Sørensen's theory that proteins in biological fluids are "reversibly dissociated component systems" held together by relatively weak secondary valencies.

J. G.

Use of Vegetable Lecithin in Noodles. H. Jesser. (*Chem.-Ztg.*, 1934, **58**, 632–634.)—For the manufacture of noodles and the like, native (German) flour is unsuitable, the products boiling badly and being of poor appearance. By addition of about 1 per cent. of plant (soya) lecithin, however, noodles closely resembling those made from imported flour are obtainable. The colour thus imparted to the product is insufficient to be confused with that of either artificial colouring matter or egg-constituents. The certain detection of vegetable lecithin presents great difficulties (*cf.* Mezger, Jesser and Volkmann, Abst., ANALYST, 1933, **58**, 555), and it is suggested that addition of a small proportion of phenolphthalein—which, in quite harmless amount, is easily detectable in the noodles—to lecithin to be used for the above purpose, might well be made compulsory.

T. H. P.

Determination of Small Amounts of Dextrose, Laevulose and Invert Sugar in the Absence and Presence of Sucrose. R. B. Whitmoyer. (*Ind. Eng. Chem., Anal. Ed.*, 1934, **6**, 268–271.)—A method for the determination of small amounts (0·5 to 2·0 mgrms.) of reducing sugars depends on the oxidation of potassium ferrocyanide to potassium ferricyanide by ceric sulphate after the ferricyanide has been reduced by the sugars in alkaline solution. The indicator used in the titration is alphazurine G, which is extremely sensitive to the least excess of ceric sulphate in acid solution. A mixture of 5 ml. of 0·8 per cent. ferricyanide solution, 5 ml. of 14 per cent. sodium carbonate solution, and 100 ml. of the sugar solution (containing up to 5 mgrms. of sugar) is heated at 80° C. for thirty minutes, cooled at 25° for five minutes, acidified with 5·7 ml. of 4·3 M sulphuric acid, and titrated with 0·01 M ceric sulphate solution; 0·545 ml. of the latter solution is equivalent to 0·2 mgrm. of invert sugar. Chlorides and tartrates do not interfere with the method, but acetates and citrates slightly affect the reduction.

W. P. S.

Determination of Aldehydes in Rancid Fats. C. H. Lea. (*Ind. Eng. Chem., Anal. Ed.*, 1934, **6**, 241–246.)—The bisulphite method may be employed for the determination of aldehydes in rancid fats. One grm. of the fat is dissolved in 2 ml. of pure benzene in a stoppered bottle, 20 ml. of 0·5 *N* sodium bisulphite solution are added, and the mixture is shaken for one hour at 20° C. in the dark. The contents of the bottle are then transferred to a tube, submitted to centrifugal action for five minutes, 15 ml. of the clear aqueous layer are placed in a flask, and the excess of bisulphite is destroyed by the addition first of *N* iodine solution, and finally of 0·002 *N* iodine solution. Should the end-point be slightly overrun, a drop or two of dilute thiosulphate solution may be added, starch indicator and at least 1 grm. of potassium iodide being present. Three grms. of sodium hydrogen carbonate are now added, and the combined bisulphite is titrated with 0·002 *N* iodine solution (*cf.* p. 697). W. P. S.

Surinam Chaulmoogra Oil. G. Sant and Stahel. (*Pharm. Weekblad*, 1934, **71**, 900–903.)—Specimens of *Taraktogenos Kurzii* grown at Paramaribo from 1905 to 1934 yielded dark-brown seeds (mean weight 2·75 grms., and dimensions 2·4 × 1·6 × 0·8 cm.) the shell of which was rejected, the residue being dried at 100° C., ground, and extracted with ether; 20 per cent. of oil, which had an acid reaction and a characteristic odour, and which became brighter at 30° C., was obtained. The following data are summarised from the authors' results, the Dutch Pharmacopoeia and Hager's *Handbuch der Pharmazeutischen Praxis*, respectively:—M.pt., 22 to 24°, 22 to 23°, 26 to 29° C.; sp.gr., 0·94 (30° C.), 0·93 to 0·945, 0·93 to 0·95 (30 to 40° C.): saponification value, 224, 195 to 215, 198 to 210; iodine value, 93, 96 to 110, 92 to 100; n_D^{40}, 1·4741, 1·4715 to 1·4750—; acid value, 1·2, —, up to 25. Thus the saponification value of the Surinam oil was much higher than the values recorded for the other oils. The fatty acids of the authors' oil solidified at 40·1° C., and had iodine value, 86·2 and mean molecular weight, 280. J. G.

Oxygen-Consuming Phenomena in Beverages. J. H. Toulouse. (*Ind. Eng. Chem.*, 1934, **26**, 769–770.)—All types of carbonated beverages examined were found to be subject to oxidative changes during storage, even if the greater portion of the actual gas was carbon dioxide; the most effective remedy is the proper adjustment or repair of filling equipment, the taking of precautions against the incorporation of air in syrups and water, and the provision of a higher carbon dioxide pressure, which seems to remove more air from the bottles. The total amount of gas in a bottle may be in the neighbourhood of 125 ml., since the normal pressure is about 5 atmospheres, and the head space some 25 ml. Analyses of the gas were made by means of a modification of the usual Orsat type of apparatus, consisting of 2 burettes (one of 100 ml. graduated to 0·2 ml., and the other of 15 ml., but over 550 mm. in length), graduated to twentieths of a ml., but with graduations nearly 2 mm. apart. The two absorption pipettes are of the bubbling type, with potassium hydroxide and alkaline pyrogallate as absorbents. About 80 ml. of gas are drawn into the larger burette and passed through the potassium hydroxide to remove carbon dioxide, and the volume of the remaining gas is determined. Fifteen ml. or, if more remain, an aliquot portion, are then passed into the smaller burette for the determination of the oxygen, and any remaining gas is calculated as nitrogen. Most of the losses of oxygen were accompanied by changes of taste or flavour, citrus fruit beverages acquiring a bitter, turpentine-like taste. The deterpenated citrus oil flavours did not change so much. Pasteurisation at 62·5° C. for 30 minutes greatly increased the rate of loss. It is significant, in view of changes in taste associated with the heating of such products, that the loss of oxygen on heating was equal to that occurring during ageing. The use of anti-oxidants is not considered feasible at present.

D. G. H.

Detection of Saccharin in Beer and other Beverages. V. Stanek and P. Pavlas. (*Woch. Brau.*, 1934, **51**, 182–183 ; *J. Inst. Brewing*, 1934, **40**, 327.)—Any carbon dioxide present in the sample is removed by warming, and 200 ml. are then acidified with 2 ml. of concentrated sulphuric acid in a flask with a wide mouth. With non-alcoholic beverages, 5 ml. of alcohol are then added, followed by 25 ml. of ether, which are poured cautiously down the side so as to form a distinct layer. The flask is closed with a cork which has been soaked in a 25 per cent. solution of calcium chloride (to keep it moist) and which carries a brass, nickel or nickel-chrome spiral. This supports in the ether layer, about 2 mm. above the water surface, a square (20 mm. side) of filter-paper pulp mixed with 30 per cent. of magnesia. After 20 hours, 20 to 25 per cent. of the saccharin present is removed on the pulp, which is then washed in 1 ml. of ether, then covered (except at the edges) by a glass slip, and dried at the room temperature; 0·001 per cent. or more of saccharin is then detectable by tasting the edges. With the exception of liquorice, which has a distinctive taste, other flavours are not absorbed. J. G.

Behaviour of Quinine Iodobismuthate with Solvents and some Applications of the Solutions. M. Picon. (*J. Pharm. Chim.*, 1934, **19**, 49–61). Whilst the solubility of quinine iodobismuthate is slight in many organic solvents, *e.g.* the lower alcohols, the paraffins and benzene homologues, pyridine, chloroform, etc., the compound dissolves readily in *cyclo*hexanone and diethyleneglycol. *Colorimetric determination of bismuth.*—Since *cyclo*hexanone is insoluble in water, it may be used to extract quinine iodobismuthate precipitated from aqueous solution, the red colour of the extract being compared colorimetrically with a standard. The method is similar in operation and equal in sensitiveness to that of Fourneau and Girard (*Bull. Soc. Chim.*, 1925, **37**, 1673), who employed tetracetylammonium iodobismuthate extracted with benzene. *Possible therapeutic application.*—Quinine iodobismuthate dissolves freely in diethyleneglycol, and solutions of sp.gr. 1·5 containing 0·55 grm. of the salt per ml. have been prepared. With a view to examining the therapeutic application of this solution, injection tests on rabbits were carried out. Whilst the gain in weight of the animals indicated that the compound was well tolerated, the results of histological tests on the organs revealed some sclerosis of the tissues, due possibly to the nature of the solvent, constituting a drawback to the use of the solution. *Solubility in acetone.*—The solubility effects in acetone are complex. With dry acetone as solvent two layers are obtained: a lower layer of a very concentrated solution shown to consist essentially of a compound of quinine iodobismuthate with six molecules of acetone, and an upper layer of a solution containing only a few units per cent. of the salt; the solubility decreases with rise in temperature. With acetone containing water, the solubility of the salt is at a maximum when 4 per cent. of water is present, and some decomposition of the salt occurs with over 10 per cent. of water in the acetone. S. G. C.

Determination of Hordenine. Y. Raoul. (*Compt. rend.*, 1934, **199**, 425–427.)—A modification of the general method of Stass has been adopted for the separation and determination of hordenine. Ten grms. of malt rootlets are extracted with 5 portions of 100 ml. of water acidified with 0·05 per cent. of sulphuric acid, and the extract is concentrated under reduced pressure, and put in a 700 ml. cylinder. A volume of ether (freed from alcohol and saturated with water) equal to 10 times that of the extract is added, and the cylinder is corked and placed horizontally on supports in such a way that an electric motor causes it to rotate on its own axis, thereby rapidly establishing solution equilibrium between the solvents without formation of an emulsion. The ethereal solution is syphoned off and washing is continued until the ether is colourless. While still in the cylinder the aqueous extract is rendered alkaline with ammonia, and deposition of the alkaloid is hastened by shaking the liquid in contact with a current of carbon dioxide. Ten successive extractions are necessary to obtain the base with an error of less than 2 per cent., and each extraction is made with 10 times as much ether as liquid to be extracted. The alkaloid is dried *in vacuo* at the ordinary temperature and purified by sublimation in a tube with a bulb (10 ml.) fitted by means of a special emery-ground joint with a conical adapter. The tube is arranged horizontally and is connected with an exhausted flask. An electric oven keeps the temperature of the tube at 105° C., and during a sublimation of 10 hours the pressure should not exceed 5 mm. of mercury. Under these conditions hordenine, even in the presence of 20 to 60 per cent. of impurities, sublimes alone, and the sublimate is a white crystalline substance of m.pt. 117·5° C. Certain malt dusts were found to contain 30 per cent. more hordenine than the amounts recorded. D. G. H.

Acid Methyl Ethers of Phosphoric Acid. V. Harlay. (*J. Pharm. Chim.*, 1934, **20**, 160–167.)—The preparation and properties of methyl- and dimethylphosphoric acids are described. The former is a dibasic acid requiring 1 mol. and 2 mols. of sodium hydroxide for its neutralisation in presence of methyl orange and phenolphthalein, respectively, whilst the latter is a monobasic acid neutralised towards phenolphthalein by 1 mol. of sodium hydroxide. These acids are not precipitated by magnesia mixture, and their presence does not interfere with the precipitation of phosphoric acid. The manner in which these observations are used to determine phosphoric, methylphosphoric and dimethylphosphoric acids (with the respective molecular weights 98, 112, and 126) present together in solution may be indicated by the following example:

Gravimetric determination of the phosphoric acid gave 0·15 grm. of H_3PO_4 per 10 ml. of the solution to be analysed; this corresponds with 1·6 ml. of *N* sodium hydroxide. Acidimetric titration of another 10 ml. required 16·4 ml. of *N* sodium hydroxide with methyl orange and 26·1 ml. with phenolphthalein. Hence, 26·1–16·4, or 9·7 ml. of the alkali represent phosphoric and methylphosphoric acids together, and 9·7–1·6, or 8·1 ml., of the alkali the methylphosphoric acid alone. The dimethylphosphoric acid corresponds with 16·4—9·7, or 6·7 ml., of *N* alkali. The numbers of grms. of the three acids present per 100 ml. of the original liquid are thus:

H_3PO_4: 0·15 × 10 = 1·5.
$H_2(CH_3)PO_4$: 0·112 × 8·1 × 10 = 9·07.
$H(CH_3)_2PO_4$: 0·126 × 6·7 × 10 = 8·44. T. H. P.

Biochemical

Silica-content of Normal and Silicotic Lungs and its Bearing on the Problem of Silicosis. F. S. Fowweather. (*J. Soc. Chem. Ind.*, 1934, **53**, 713–716.)—The chemical findings of examinations, over a period of more than two years, of the lungs of miners, asbestos workers, sand-blasters, and others thought liable to silicosis, are discussed. The dry lung-tissue of five adults who had not been exposed to dangerous dusts showed from 3·95 to 4·66 per cent. of ash, the average being 4·42; the silica-content ranged from 0·12 to 0·20 per cent., with an average of 0·163. In one exceptional case, that of a railwayman exhibiting marked anthracosis, the figures for ash and silica were within the above limits. The other cases considered are arranged in two ways, namely, according to the amounts of silica in the lungs and according to the occupations of the patients. The data collected show definitely that no connection exists between the content of silica in the lungs and the degree of silicosis observed. Hence, it seems, either that silicosis is determined, not by the amount but by the nature of the silica, some forms of which are far more potent silicotic agents than others, or that silicosis is determined to some extent by certain conditions prevailing in the body of the patient. As regards the second alternative, the individual powers of resistance must play an important part, and, in presence of pre-existing weakness or disease of the lungs, the harmful effect of silica would be accelerated and aggravated. Of all the cases investigated, about 50 per cent. showed silicosis associated with tuberculosis, but in about 10 per cent., not only was tuberculosis absent, but no evidence of bronchiectasis, bronchitis, pneumonia, abscess or gangrene was revealed. The conclusion is drawn that the infective factor is an important one in the production of silicosis.

With reference to the varying effects of silica in different forms, it is pointed out that the lungs of coal-miners who have had silicosis show relatively large proportions of silica, whereas with sand-blasters, stonemasons, and asbestos workers, silicosis is observed with much smaller amounts of silica in the lungs. Of special interest is the group of asbestos workers, and complete data are available in one instance where other complications were absent. Subtraction of the amounts of ash and silica found in normal lungs from those found in this case shows that the excess amount of ash is represented wholly by silica. As the material inhaled was a complex silicate, the asbestos must have undergone decomposition in the lungs, with deposition of the silica and removal of the metallic oxides. Since six years elapsed after the man ceased work before he died, it appears that the decomposition of the asbestos, which had been proceeding during the eleven years he was employed, was continued and brought to completion after his retirement.

Other evidence supporting this view is mentioned, and it is pointed out that, where long intervals pass since exposure to asbestos, the amount of silica actually found will not give a correct indication of the silica which has been in the lungs, as much must have been transported. The slight alkalinity of the blood and tissue-fluids, and the increased flow of such fluids to the affected parts caused by the inflammatory reactions promoted by infective conditions, would favour decomposition of the silicates. The most potent producers of silicosis should, therefore, be the soluble alkali silicates. T. H. P.

Body Fats of the Hen. T. P. Hilditch, E. C. Jones and A. J. Rhead. (*Biochem. J.*, 1934, **28**, 786–795.)—The examination of the body fats of the hen showed that these possess specific characteristics which distinguish them from those of quadrupeds, fishes or marine mammals. These fats fall into that broad group of depot fats, found in non-aquatic animals, which contain only 30 to 35 per cent. of saturated acids. The depot fats of the hen yield component fatty acids, about 65 per cent. of which belong to the C_{18} series, and these are mainly oleic acid (35 to 38 per cent.) and linolic (20 to 22 per cent.); no evidence of acids more unsaturated than linolic was observed in this group. There are also small amounts of the $C_{20\,22}$ acids and about 7 to 8 per cent. of palmitoleic acid, and these cause the fats to possess features analogous to those possessed by fats from marine animals, although the hen fats are really nearer to the rodent fats than to fats from aquatic fauna. Up to the present, palmitoleic acid has been reported only in the fats from aquatic animals, rat body fats, fat from diphtheria bacilli, and now from hen body fats. Although the specific type of a depot fat appears to depend on the biological species, it is found that the body temperature may be a secondary factor, for the hend, with a uniformly high body temperature, has almost identical fats in various parts of its body, whereas in the pig the nature of the fats changes in going from the epidermis to the centre of the body. The presence of traces of myristic acid and 5 to 7 per cent. of stearic acid is regarded as a specific feature; but the molecular percentage of palmitic acid (25 to 30) is the same as that found in the fat of all land animals. The amount of palmitoleic acid is independent of the diet received by the birds. S. G. S.

Absorption of Manganese by Plants. C. Olsen. (*Compt. rend. Lab. Carlsberg*, 1934, **20**, 2.)—As a result of the investigations carried out it appears that land plants under natural conditions absorb increasing amounts of manganese with increasing hydrogen ion concentration, and also with increasing concentrations of manganous sulphate, so that most manganese is absorbed from acid soils. Grown in a basic soil plants contain, as a rule, only a few mgrms. of manganese per 100 grms. of dry leaf material, but this amount may be increased to over 200 mgrms. in a strongly acid soil, and in such a soil the proportion of manganese may exceed that of iron. In water cultures the optimum p_H value for manganese absorption is 6 to 7, and increasing amounts are absorbed with increased concentration of manganous sulphate (from 0 to 2·5 mgrms. $MnSO_4, 4H_2O$ per litre). At this higher concentration a poisoning effect was observed on *Lemna polyrhiza*, the growth of which was inhibited. Absence of manganese usually results in the development of brownish streaks or spots on the leaves (grey speck disease), which die away in patches. The high proportion of manganese found in water and swamp plants is probably due to the comparative lack of oxygen in such conditions, and the possibility of the manganese being present as manganous salt, in which form only it appears to be absorbed. Manganous salts are stable in acid soils, whilst in neutral or basic soils the manganese is presumably oxidised to manganese dioxide, and is thus no longer available to the plants. D. G. H.

Relation of the Colour and Vitamin *A* Content of Butter to the Nature of the Ration Fed. (I) Influence of the Ration on the Yellow Colour of Butter. S. J. Watson, G. Bishop and J. C. Drummond. (II) The Carotenoid and Vitamin *A* Contents of Butter. A. E. Gillam and I. M. Heilbron. (*Biochem. J.*, 1934, **28**, 1076–1085.)—Artificially dried grass and A.I.V. fodder were used in a series of experiments on Shorthorn and Ayrshire cows. A.I.V. fodder is produced by a modification of the ensilage process, in which the forage crop is treated with dilute mineral acids so that an acidity of p_H 3 to 4 is developed, and then stored in containers without access to air. By this means the temperature does not rise appreciably, and the carotene content of the forage is preserved to a large extent. When 10 or 25 per cent. of the foodstuffs in a normal winter ration for Shorthorn cows was replaced by artificially dried grass no appreciable change in the amount of yellow colour in the butter-fat was noticed. When 50 per cent. of artificially dried grass was added, there was a marked increase in the yellow colour of the butter-fat. The inclusion of 40 lb. per head daily of A.I.V. fodder raised the yellow colour of the butter-fat to a high level, comparable with that obtained on best pasture. The carotene and xanthophyll contents of the butter were trebled and the vitamin *A* content doubled, in comparison with butter from the control group of cattle. When Ayrshire cows were used instead of the Shorthorn cows, it was found that for a normal winter ration the yellow colour of the butter was below that of Shorthorns. For each breed there appears to be a "ceiling" level for both colour intensity and vitamin *A* content, and no excess of fodder rich in carotene will cause these values to rise above this level. This "ceiling" value is much lower for Ayrshires than for Shorthorns, but 40 lb. per head daily of A.I.V. fodder caused this value to be reached. In spite of the colour differences there may, however, be little difference between the vitamin *A* content of the butter from each breed. Goats' butter, which is almost colourless, has practically the same vitamin *A* content, although the carotene content may be only 5 per cent. of that of cows' butter. S. G. S.

Influence of the Solvent on the Vitamin *A* Activity of (a) Carotene, and (b) Cod-liver Oil. F. J. Dyer, K. M. Key and K. H. Coward. (*Biochem. J.*, 1934, **28**, 875–881.)—The biological activity of the provisional International Standard for vitamin *A* may be greatly influenced by the oil used for its solution. When arachis oil was used, the standard had 5 to 6 times the potency of the same strength solution in hardened cotton-seed oil or in ethyl laurate. Solutions of the same strength in arachis oil and in coconut oil had the same vitamin *A* potency. Two samples of coconut oil gave solutions of the same potency, but with a third sample the result was doubtful. This effect of the solvent oil may also be apparent if the oil is used to dilute cod-liver oil. When a cod-liver oil was dissolved in an inactive coconut oil, the resulting solution was about three times as potent as when hardened cotton-seed or olive oil was used. The comparison between a cod-liver oil and the Standard was the same when both were dissolved in arachis oil or both in coconut oil. A sample of β-carotene showed a vitamin *A* activity 175 per cent. that of the International Standard. In one case it was found that the yellow colour of different solutions of the Standard did not correspond with the vitamin *A* activities of those solutions. S. G. S.

Ascorbic Acid Content of Certain Citrous Fruits and some Manufactured Citrous Products. A. L. Bacharach, P. M. Cook and E. L. Smith. (*Biochem. J.*, 1934, **28**, 1038–1047.)—Values are given for the ascorbic acid content of the juice of individual fruits of oranges, from nine different sources; of tangerines, from three sources; and of lemons, from four sources. Determinations were made by titration with 2:6-dichlorophenolindophenol in acid solution, and in many cases with iodine also. The two methods are in good agreement. Thirty-nine oranges gave values varying from 0·22 to 0·89 mgrm. of ascorbic acid per ml. of juice, with a mean of 0·51 mgrm. per ml. Nine tangerines gave extreme values of 0·10 and 0·78 mgrm. per ml., with a mean of 0·37 mgrm. per ml. Fifteen lemons gave values between 0·47 and 0·73 mgrm. per ml., with a mean of 0·64 mgrm. per ml. Fruits from the same consignment gave values which varied considerably. Storage of the fruit for one month caused an average loss of activity of 20 per cent. for oranges and 6 per cent. for lemons. Concentrated orange juice, when examined by both chemical and biological methods, showed very little loss of activity due to concentration and subsequent storage. Eleven varieties of marmalade were also examined and, except for three varieties which gave a negative test, these contained from 0·06 to 0·14 mgrm. of ascorbic acid per grm. The richer kinds were those apparently containing a large amount of peel. The flavedo of citrous fruit was richest in reducing power, and the albedo the next richest; the juice was poorer in ascorbic acid than the peel, whilst the pips contained no demonstrable quantity. The authors suggest that, in view of the variable antiscorbutic potency of lemon juice, the international unit of vitamin *C* should be redefined as the vitamin *C* activity of some definite weight of ascorbic acid. S. G. S.

Physiological Action of Ascorbic Acid and some Related Compounds. V. Demole. (*Biochem. J.*, 1934, **28**, 770–773.)—Doses of *l*-ascorbic acid up to 5 grms. per kilo. in one dose, or 12 grms. per kilo. in all were tolerated in the animals without symptoms of any kind. Histological examination of the organs failed to show changes in the kidney, liver, heart, or lungs, and no evidence of hypervitaminosis *C* was obtained. The administration of 0·1 grm. of ascorbic acid per kilo. subcutaneously to a dog was followed by the excretion of 75 per cent. of this in the urine within nine hours. It was also found that the urine of animals which received large doses of ascorbic acid was capable of curing scurvy in guinea pigs, if given in doses of 0·2 to 1 ml. daily. Synthetic *l*-ascorbic acid showed no difference in biological activity from that derived from paprika, but *d*-ascorbic acid was inactive in doses of 20 mgrms. daily. Of the other isomerides and homologues of ascorbic acid, only *d*-erythro-3-ketohexonic acid showed any definite antiscorbutic activity, and only about one-twentieth that of *l*-ascorbic acid.

S. G. S.

Influence of Vitamin *C* (Ascorbic Acid) on Plant and Animal Amylases. A. Purr. (*Biochem. J.*, 1934, **28**, 1141–1148.)—The *β*-type of amylase which occurs in the inactive form in animal organs can be activated by vitamin *C* (ascorbic acid). The action of vitamin *C* on amylases of plant origin is the reverse of this, for on the *α*-amylase it has no action, and on the *β*-type it has an inhibitory effect. During the study of the relation between amylase activity and the growth of grain the conclusion was reached that the amylase relationships are the same as those of sprouting grain. At the end of the growth period the *α*-amylases become inactive, and it is at this stage that vitamin *C* was found by Virtanen (*Biochem. Z.*, 1933, **267**, 179) to decrease, and this is correlated with the fact that oxidised vitamin *C* inhibits plant *α*-amylase, but has no action on the *β*-form.

S. G. S.

Vitamins in Canned Foods. Calcium and Vitamin *D* in Foods. E. F Kohman, N. H. Sanborn, W. H. Eddy, and C. Z. Gurin. (*Ind. Eng. Chem.*, 1934, **26**, 758–761.)—In order to test the widespread statement that a certain amount of raw food is necessary to optimum well-being, a large number of experiments were conducted with rats, reared through 5 generations on respectively (*a*) raw, (*b*) home-cooked, and (*c*) canned foods, without milk. The foods used were various types of meat, a few marine products, and most of the common fruits and vegetables. Weight at birth and weaning were progressively higher on *a*, *b* and *c*; subsequent growth much the same for *a* and *b*, but better on *c*. The number per litter was smaller on *a*, and slightly smaller on *b* than on *c*. Deaths before weaning were higher on *a*, and slightly higher on *b* than on *c*. The rats on the *a* diet had enlarged caeca, in comparison with those on *c*. The bone-ash of the tibiae of a considerable number of animals at 60 days averaged: *a*, 45·5; *b*, 39·1; and *c*, 49·9 per cent. Addition of milk to the diet increased the ash-content in every case. A mixture of 5 canned foods was adjusted to the calcium to phosphorus ratio of the Steenbock diet by addition of calcium salts, and cod-liver oil added to this had no effect when fed to the rats. The authors conclude that ordinary foods contain significant amounts of vitamin *D*.

D. G. H.

Toxicological

Comparative Toxicity of Fluorine Compounds. M. C. Smith and R. M. Leverton. (*Ind. Eng. Chem.*, 1934, **26**, 791–797.)—The lethal and chronic toxic levels of fluorine for rats have been studied, and a comparison made of the effects of the following compounds of fluorine: sodium, potassium, ammonium and calcium fluorides; cryolite; and barium, sodium and potassium fluosilicates. Wide differences in toxicity have been found when the effects upon growth, food utilisation and damage to teeth are considered, which may, or may not, be due to the differences in solubility. But in every case the effect on the teeth was observable at concentrations far below those accounting for any other signs of ill-health, that is when 1 mgrm. of fluorine per kilo. of body weight was fed daily, and at this low level the source of the fluorine makes no difference. With sodium, potassium or ammonium fluoride, or barium or sodium fluosilicate, an incorporation in the diet at a 0·0226 percentage level resulted in retardation of the growth rate during a six-weeks' experimental period, and a decrease in the efficacy of utilisation of food. About 10 times as much fluorine combined as cryolite, and 20 times as calcium fluoride, were required to produce similar slight effects. With the first set of compounds a concentration of fluorine of 0·0904 per cent. caused death in 9 to 11 days, 3·6 per cent. was necessary with cryolite and 5·4 per cent. with calcium fluoride. Fluorine is more toxic to the teeth of human beings than to those of rats, and as little as 1 p.p.m. of fluorine in drinking water will cause mottled enamel in the permanent teeth of a child while they are in process of formation. Apples sprayed with barium fluosilicate have shown an average fluorine residue, before washing, of 5·6 p.p.m., so that such a spray may be a distinct source of danger. There was no evidence of specific damage to the reproductive organs. D. G. H.

Determination of Benzene in Toxicology. I. Preliminary Study of the Colorimetric Determination of *m*-Dinitrobenzene. M. Péronnet. (*J. Pharm. Chim.*, 1934, **20**, 145–149.)—The violet colour given by *m*-dinitrobenzene with a reducing sugar in alcoholic solution may be utilised for the determination of the nitro-compound. For quantities of 0·0002 to 0·02 grm. of *m*-dinitrobenzene in 20 ml. of the final solution, the depth of colour is accurately proportional to the concentration of the substance, and results exact to within 1 per cent. are obtainable. The following conditions must be observed:—The alkalinity of the liquid must correspond with sodium hydroxide of about one-eighth normality, the concentration of the alcohol must be from 65 to 75 per cent. (by vol.), and the reaction must proceed for 15 to 20 minutes at 25° C.; as carbohydrate, laevulose is found suitable. These conditions are fulfilled by mixing 10 ml. of a solution of the *m*-dinitrobenzene in 95 per cent. (by vol.) alcohol, 1 ml. of 10 per cent. sodium hydroxide solution, 5 ml. of 1 per cent. laevulose solution, and 4 ml. of 95 per cent. alcohol. The colour is compared with those given by standard *m*-dinitrobenzene solutions in the usual way. T. H. P.

Bacteriological

Effect of Exposure to Low Temperatures on the Number of Bacteria in Fish Muscle. M. M. Stewart. (*J. Soc. Chem. Ind.*, 1934, **53**, 273–278T.)—Owing to the use of a varying mixed bacterial flora, experiments to determine the efficiency of exposure to low temperatures as a means of preserving foods have led to discrepant results. In the present series of experiments the changes occurring in the numbers of mixed organisms in haddock's muscle have been observed throughout varying periods of storage at temperatures varying from —1·2° to —12° C. Haddock's muscle inoculated with a mixed flora of organisms from the surface slime was used in preference to pure cultures on artificial media in order to approximate to commercial conditions. The results obtained are largely in agreement with those of previous workers and show that exposure to low temperature causes an initial decrease in the numbers of organisms in the muscle to a degree varying with the temperature. Between —1·2° and —3° C. the decrease is comparatively slight and, after a lag-phase of 1 to 15 days in the different experiments, rapid multiplication of the organisms occurs. With supercooled tissue at —1·2° or —2° C., indications, but not definite proof, of more rapid growth than with frozen tissue were obtained. At —4° C. the initial decrease becomes more marked and the lag-phase more prolonged, from 35 to 50 days elapsing before growth took place. At —6° C. the number of bacteria was much less after 60 to 80 days than in the beginning. At —12° C. the initial decrease was still more pronounced, and no sign of growth was observable after 210 days. Thus, over long periods of storage, temperatures in the neighbourhood of —12° C. are necessary to inhibit bacterial growth completely. For periods common under commercial conditions, —6° C. would probably suffice, but some of the organisms able to grow at this temperature are chromogenic and hence undesirable. In these experiments the storage of fish has been considered solely from the standpoint of bacterial decomposition. Other changes of chemical, physico-chemical, or enzymic (rancidifying) nature are equally important, and it is essential that the temperature of storage should be low enough to inhibit such changes also. Of 29 cultures of micro-organisms which remained alive on plates inoculated with haddock's muscle and kept at —12° C. for 3 months, 9 were *Achromobacter*, 13 *Flavobacter*, 4 *Micrococci*, and 3 yeasts. Since *Flavobacter* species formed only 11 per cent. of the organisms present originally in the slime of fresh haddock, it appears that this genus shows the greatest resistance to prolonged exposure to low temperatures.

T. H. P.

Organic Analysis

Furoic Acid as an Acidimetric Standard. H. B. and A. M. Kellog. (*Ind. Eng. Chem., Anal. Ed.*, 1934, 6, 251.)—Recrystallised and sublimed furoic acid, which melts at 131° C., is recommended for use in standardising alkali solutions. The acid is very slightly hygroscopic and should be fused in a platinum basin at a temperature not exceeding 142° C., just before it is required for use.

W. P. S.

Volumetric Determination of 5-Bromo-2-Furoic Acid with Standard Bromate Solution. E. E. Hughes and S. F. Acree. (*Ind. Eng. Chem., Anal. Ed.*, 1934, 6, 292–293.)—A known quantity of the sample is placed in a special side-arm titration flask containing 200 ml. of 3 per cent. hydrochloric acid; 25 ml. of 0·1 *N* bromate bromide solution are introduced into one of the side arms, and 10 ml. of 10 per cent. potassium iodide solution into the other arm. The flask is closed, the contents brought to 21° C., and the bromate solution is then added to the acid by tilting the flask. After about ten minutes the iodide solution is introduced, the contents of the flask are well mixed, and the liberated iodine is titrated with 0·1 *N* thiosulphate solution.

W. P. S.

Magnesium for Grignard Reagents. N. W. Cusa and F. S. Kipping. (*J. Soc. Chem. Ind.*, 1934, **53**, 213–214T.)—In the preparation of magnesium *cyclo*hexyl bromide from theoretical proportions of metal and halide, it was found that the yield of Grignard reagent is less than 40 per cent., owing to the formation of di*cyclo*hexyl. Although similar low yields are on record, certain American workers have obtained yields of 92 per cent. for the bromide, and 96 per cent. for the chloride (*cf.* Gilman and Zoellner, *J. Amer. Chem. Soc.*, 1931, **53**, 1945); for high yields it is necessary, especially in the former case, to add the halide very slowly to the magnesium and ether. The difference was eventually traced to the magnesium used, but it was not possible to ascertain what are the impurities which, by their absence or presence, depress the yields. The impurities in the American sample were aluminium, 0·50; silica, 1·10; iron, manganese and copper, 0·05 per cent. each; and traces of grease; whilst that used by the authors contained less than 1 per cent. of impurity, consisting of 0·6 per cent. of combined carbon and "a trace of zinc, a faint trace of iron and aluminium, a very faint trace of heavy metals, silica and phosphorus." J. G.

Quinone as a Reagent for Amines. M. Foucry. (*J. Pharm. Chim.*, 1934, **126**, 116—118.)—If 5 ml. of a solution consisting of 5 parts of acetic acid and 1 part of quinone, dissolved in 100 parts of alcohol, are added to 5 ml. of an aqueous, neutral, or slightly acetic acid solution of an amine, and the mixture is boiled and left to cool, a red colour is immediately formed or in very dilute solutions develops during cooling. Mineral alkaline salts must be absent. Concentrated ammoniacal solutions give colours similar to those produced by amines, but dilute solutions give no colour. The reaction may be used for such products as hydroxylamine, aniline, phenylhydrazine, piperazine, hexamethylene-tetramine, and pyridine. Pyramidon may thereby be distinguished from antipyrine. Certain amino acids, such as glycocoll and alanine, give a positive reaction, but others, such as cystine, taurine and tyrosine, give no reaction. Novocaine may also be distinguished from stovaine, particularly if 1 drop of sulphuric acid (sp.gr. 1·57) is added to the solution before the reagent, and the mixture is boiled. Under these conditions urotropine, alanine and glycocoll no longer give the reaction. D. G. H.

Determination of Citrate. W. F. Bruce. (*Ind. Eng. Chem., Anal. Ed.*, 1934, **6**, 283–285.)—The method depends on the oxidation of citric acid by potassium permanganate in the presence of mercuric sulphate; the insoluble precipitate formed is weighed. Five ml. of the test solution, containing a few mgrms. of citric acid, are treated with 1 ml. of 10 per cent. barium acetate solution, 4 drops of saturated barium hydroxide solution and 10 ml. of 95 per cent. alcohol; after ten minutes the precipitate is separated by centrifugal action, washed three times with 3 ml. of 50 per cent. alcohol containing 1 per cent. of barium acetate, and dissolved by heating in a mixture of 3 ml. of water and 0·16 ml. of 85 per cent. phosphoric acid. The hot solution is treated with 1 ml. of mercuric sulphate solution (50 grms. of mercuric oxide and 200 ml. of 96 per cent. sulphuric acid per litre), diluted to 10 ml. with water and centrifuged, and the solution is filtered. Eight ml. of the filtrate, 0·2 ml. of mercuric sulphate solution and 1 ml. of water are heated at 85° C. for one minute, and a drop of 3 per cent. hydrogen peroxide is added, followed by 1 per cent. potassium permanganate solution, which is added at the rate of one drop in ten seconds until a pink colour persists for ten seconds. One drop of hydrogen peroxide is then added, the mixture is cooled and centrifuged, and the precipitate is washed three times with 3 ml. of 50 per cent. alcohol, dried at 100° C., and weighed. The weight of the precipitate is multiplied by 10/8 to correct for the fraction of the solution taken, and then compared with the weight of precipitate yielded by a known amount of citric acid. For instance, 2 mgrms. of citric acid yield 4 mgrms. of precipitate, 4 mgrms. of acid 12 mgrms., and 8 mgrms. 26 mgrms. Formic, acetic, succinic, malic, lactic, and tartaric acids do not interfere with the determination. W. P. S.

Determination of Malic Acid in Plant Tissue. G. W. Pucher, H. B. Vickery and A. J. Wakeman. (*Ind. Eng. Chem., Anal. Ed.*, 1934, **6**, 288–291.)—Malic acid when oxidised in acid solution at 20° C. by potassium permanganate in the presence of potassium bromide yields a bromine compound which is volatile in steam. Citric acid, if present, yields pentabromoacetone, but this may be removed by extraction with petroleum spirit before the steam distillation. The volatile substance gives a precipitate when treated with dinitrophenylhydrazine in acid solution; the precipitate may be collected on a filter and then dissolved in pyridine. If the pyridine solution is diluted with water and rendered alkaline with sodium hydroxide a blue colour develops which is suitable for spectrophotometric measurement. The intensity of the colour is proportional to the amount of malic acid present over a range of 0·1 to 2·5 mgrms., and is stable for several hours. The same bromo-compound is formed from both optically active and inactive malic acid. Acetic acid, lactic acid, fumaric acid, succinic acid, pyruvic acid, tartaric acid, maleic acid, glycollic acid, and glyoxylic acid do not yield the volatile compound. W. P. S.

Comparative Action of Periodic Acid on Certain Hexoses and on the Artificial Glycosides derived therefrom. H. Hérissey, P. Fleury and (Mlle) M. Joly. (*J. Pharm. Chim.*, 1934, **20**, 149–159.)—In cold aqueous solution, periodic acid is reduced by glucose, mannose or galactose thus: $C_6H_{12}O_6 + 5HIO_4 = 5HIO_3 + H.CHO + 5H.CO_2H$. Under similar conditions, the methyl and ethyl glycosides of these sugars consume only 2 (in place of 5) atoms of oxygen, no formaldehyde being formed. These results confirm the stability of the 1:5 oxygen-atom bridge in such glucosides. T. H. P.

Determination of Hexamethylenetetramine by Precipitation of its Double Uranyl Sulphate. M. Foucry. (*J. Pharm. Chim.*, 1934, **20**, 168–170.)—This double sulphate, $UO_2SO_4, N_4(CH_2)_6H_2SO_4$, which separates in cubical crystals and leaves a residue of U_3O_8 on ignition, is very slightly soluble in water, especially in presence of free sulphuric acid, and is insoluble in ether, 95 per cent. (by vol.) alcohol, or 50 per cent. alcohol acidified with sulphuric acid. For the detection or determination of hexamethylenetetramine (urotropine) use is made of a reagent prepared by adding 30 ml. of 66 per cent. sulphuric acid, gradually and with cooling, to 170 ml. of 95 per cent. alcohol, and dissolving 10 grms. of uranyl nitrate in the mixture. To detect urotropine in a liquid, this is treated with an equal volume of the reagent. With moderate concentrations of urotropine, precipitation of the double salt is immediate; with low concentrations the precipitation requires time and only after 10 minutes can absence of precipitate be taken to indicate absence of urotropine. The solution used for the determination should contain not more than 5 grms. of urotropine per litre. The liquid is treated with an equal volume of the reagent and left for 1 hour, after which the clear liquid is decanted on to a tared filter, and the precipitate is afterwards transferred to this filter by means of a minimum quantity of 50 per cent. alcohol containing 5 per cent. of its volume of 66 per cent. sulphuric acid. The precipitate is washed first with 95 per cent. alcohol until free from soluble sulphate and then twice with anhydrous ether. After evaporation of the residual ether the precipitate is dried for 10 minutes at 80° to 100° C. and weighed. The weight of urotropine is obtained by multiplying the weight of the precipitate by 0·232. The determination is not disturbed by mineral or organic acids, and no interfering constituents have been found in the various pharmaceutical urotropine preparations examined.

T. H. P.

Some Properties of Chlorinated Wool and the Determination of Damage in Chlorinated Knitted Woollen Goods. S. R. Trotman, H. S. Bell and H. Saunderson. (*J. Soc. Chem. Ind.*, 1934, **53**, 267–273T.)—The usual method of ascertaining the wearing power of chlorinated woollen goods by microscopic examination of fragments of yarn from different parts of the fabric is not entirely satisfactory, for various reasons. With the object of arriving at a supplementary test, the authors have made quantitative dyeing tests with scoured wool and with the same wool after chlorination in such ways as to cause damage to various extents. With acid dyestuffs, like indigo carmine, moderate chlorination of the wool causes an increase in the quantity of dyestuff absorbed, whereas over-chlorination appears to reduce it. Commercial goods are almost always over-chlorinated (over 50 per cent. of damaged fibres), and the chlorinated wool dyes much more rapidly than the unchlorinated and assumes a deeper shade. Neutral-dyeing acid dyestuffs, and also basic dyestuffs act in much the same manner. All the direct dyestuffs tried dye chlorinated wool from a cold neutral or alkaline (with sodium carbonate) bath, but leave the unchlorinated wool quite white. The behaviour of vat dyestuffs was also examined. The most suitable dyestuffs for the purpose in view are those of acid or basic character, and extensive experiments made with Kiton Red G, indigo carmine, and methylene blue lead to the following optimum conditions for the test:—Two grms. of the sample are treated for 90 minutes at atmospheric temperature with 100 ml. of 0·005 *N* hydrochloric acid containing 0·01 millimol. of Kiton Red G. The liquor is then filtered through glass wool, and an aliquot part of the filtrate is matched against a standard solution containing 0·01 millimol. of the dyestuff per litre. The number of millimols. absorbed per 100 grms. of wool is then calculated. It is of advantage to unravel web before testing. In preparing the standard dyestuff solution, allowance must of course be made for the salts and moisture always present in commercial acid dyestuffs. As a means of distinguishing between good and bad samples of wool, this method gives satisfactory results, but for percentages of damage exceeding 50 (as determined under the microscope), the absorption of the dyestuffs does not proceed in proportion to the extent of the damage. Indigo carmine may be used in place of Kiton Red G, the residual unabsorbed dyestuff being determined by titration with permanganate. The indications are not the same with the two, but in each case absorption increases progressively with the degree of chlorination.

As chlorination of wool proceeds, the affinity for water at first increases and later decreases. Further, chlorinated wool is more readily attacked by sodium carbonate solution, but neither its solubility in this solution nor the quantity of the solution retained is related directly to the degree of damage. T. H. P.

Inorganic Analysis

Use of Activated Carbon for Removal of Small Quantities of Arsenic Chloride from Hydrochloric Acid. S. E. Coalstad. (*Chem. and Ind.*, 1934, **53**, 632–633.)—Concentrated sulphuric acid is added, little by little, to the hydrochloric acid to be purified, contained in a large earthenware Woulff's bottle. The hydrogen chloride given off is passed up through a lead absorption tower containing wood charcoal activated by the method recommended by Holmes (*Laboratory Manual of Colloid Chemistry*), and the emerging gas is absorbed in water. Preliminary removal of sulphur dioxide from the hydrochloric acid to be purified may be effected by the addition of potassium permanganate; the bulk of the chlorine which is simultaneously produced is removed by means of a stream of air, and the last traces of chlorine are eliminated by the addition of sufficient ferrous chloride. An alternative method for removing arsenic from hydrogen chloride by bubbling it through hypophosphorous acid solution has not been found to be completely effective, and it suffers from the drawback that the hydrogen chloride becomes contaminated with traces of phosphorus in the form of phosphine, which is a product of the slow decomposition of hypophosphorous acid. S. G. C.

Quantitative Determination of Arsenic by Marsh's Process. J. Gangl and J. V. Sanchez. (*Z. anal. Chem.*, 1934, **98**, 81–96.)—A detailed description is given of a procedure and apparatus for quantitatively volatilising and recovering arsenic in Marsh's test. The solution is reduced with powdered zinc, and subsequently boiled for the expulsion of the dissolved arsine. Decomposition of the gas is effected in a spiral silica-glass tube, 1 mm. in internal diameter. The arsenic mirror is dissolved in iodine monochloride, and the liberated iodine is titrated with potassium iodate. For full details the original paper should be consulted. W. R. S.

Nephelometric Determination of Arsenic. A. Amati. (*Ann. Chim. anal.*, 1934, **16**, 312).—The turbidity of elemental arsenic, formed by the reducing action of hypophosphorous acid on arsenic compounds in concentrated hydrochloric acid solution, may be determined by means of the Pulfrich nephelometer. The sensitiveness is 3×10^{-5} grm. of arsenious oxide per cent. No practical details are given. S. G. C.

Use of Solid Carbon Dioxide in the Determination of Tin. H. I. White. (*Ind. Eng. Chem., Anal. Edit.*, 1934, **6**, 234.)—The determination is conducted in the usual way up to the point where carbon dioxide is passed through the solution.

At this point, about 0·5 cubic inch of solid carbon dioxide is added. Besides yielding an atmosphere free from oxygen, the solid carbon dioxide cools the solution rapidly. W. P. S.

Determination of Tantalum and Niobium in Wolframite. J. A. Tschernichow and M. P. Karsajewskaja. (*Z. anal. Chem.*, 1934, **98**, 97–107.)—The finely-ground mineral (10 grms.) is attacked with hydrochloric acid, the solution is evaporated, boiled with nitric acid and diluted, and the yellow residue is collected and washed with hot water. The tungstic acid is dissolved in a mixture of 40 ml. of 10 per cent. ammonia and 20 ml. of saturated ammonium nitrate solution. The residue from the extraction is ignited and again submitted to the above process. The ignited residue from the second extraction is treated with hydrofluoric and sulphuric acids, evaporation with the latter acid is repeated, and the almost dry residue is digested with 10 per cent. hydrochloric acid. The liquid is made slightly ammoniacal, and the precipitate (containing the whole of the earth acids) is collected, washed with ammonium nitrate, ignited and fused with bisulphate. The melt is dissolved in tartaric acid, and the solution is freed from the metals of the hydrogen sulphide and ammonium sulphide groups. The filtrate is treated with cupferron, and the ignited precipitate of impure pentoxides is weighed. Two small portions (0·001 to 0·005 grm.) are weighed off and tested colorimetrically, the one for titania, the other for tungstic oxide. If the latter preponderates, it is separated from the earth acids (in the bulk of the precipitate), by Schoeller and Jahn's bicarbonate hydrolysis (ANALYST, 1927, **52**, 511); the precipitated earth acids are freed from titania, if necessary, by Schoeller's pyrosulphate tannin process (*ibid.*, 1929, **54**, 455). If titania preponderates, it is first removed by the pyrosulphate tannin process, and the tungstic oxide next by bicarbonate hydrolysis. The separation of tantalum from niobium in the purified pentoxides is effected by the improved tannin procedure (*ibid.*, 1932, **57**, 750). The tantalum and niobium fractions should be tested colorimetrically for titania (*ibid.*, 1927, **52**, 632) and tungstic oxide (*infra*). The above method is recommended for mineralogical and geochemical work.

The colorimetric determination of tungstic oxide in the pentoxides (0·003 to 0·01 grm.) is carried out by fusion with 1·3 grm. of sodium carbonate, solution of the melt in 15 ml. of warm water, filtration (if necessary), and dilution to 50 ml. Twenty ml. are pipetted into a 50-ml. flask, treated with 2·5 ml. of 25 per cent. potassium thiocyanate solution, and made up to the mark with a solution of 10 grms. of stannous chloride in 90 ml. of strong hydrochloric acid. The colour is matched after 45 to 60 minutes against those of a standard scale prepared from a sodium tungstate solution (0·0002 grm. WO_3 per ml.), diluted with 0·5 *N* sodium carbonate solution to 20 ml. and treated exactly like the unknown solution; standards and assay should be done at the same time. W. R. S.

Diphenylcarbazide as Indicator in the "Mercurimetric" Determination of Chloride. J. Trtílek. (*Ann. Chim. anal.*, 1934, **16**, 329.)—When the chloride ion is titrated with mercuric nitrate solution, undissociated mercuric chloride is formed, and diphenylcarbazide serves as indicator, producing a bluish-violet colour with mercuric ions added beyond the equivalence point. For satisfactory end-points, the neutral chloride solution to be titrated should be acidified with not more than 1 to 3 ml. of 0·2 *N* nitric acid for each 100 ml., and 0·5 ml. of alcoholic diphenylcarbazide solution (1 to 2 per cent.) should be added as indicator. In more strongly acid solutions the end-point is less definite, and over-titration may result. S. G. C.

Microchemical

Note on Schöbel's Heating Block for the Pregl Micro-Carbon-Hydrogen Determination. H. Lieb. (*Mikrochem.*, 1933–34, 14, 263–264.)—Various types of heating blocks, or constant-temperature heaters, to maintain the lead peroxide of the combustion tube filling in the carbon and hydrogen determination between the temperatures of 170° and 200° C., have been tested in the Pregl laboratories. Verdino's block (*Mikrochem.*, 1931, 9, 123; Abst., ANALYST, 1932, 57, 199) is especially constructed to prevent the liquid (cymene or decalin) heated in the block, from boiling over, but has the disadvantage that the liquid rapidly tends to gum formation, probably owing to the action at the metal surface, and it is also difficult to know how much liquid is in the base portion of the heater, and whether it is boiling evenly. Schöbel's heating block (*Schott u. Gen. Jenaer Glaswerk, Katalogblatt* 4671/31 Gi 380), made of Jena hard glass, has none of these disadvantages. The heater is made of the same dimensions as the Pregl heater—a cylinder 7 cm. long and 3·5 cm. in diameter, the inner cylinder being made to fit outside the combustion tube. A glass chimney, 35 cm. long, fits on to a neck on the outside of the cylinder. The heating may be carried out electrically or by means of the usual micro-burner. When a micro-burner is used the apparatus is fitted in a semi-cylindrical support of sheet steel or brass, lined with asbestos paper, the whole being attached in the usual position above the burner. The metal contacts for the constrictions in the capillary tubes are attached to the metal support. This type of constant temperature heater has been in use in the Pregl laboratory for two years. J. W. M.

Methods for the Micro-Determination of Non-Protein Nitrogen and Urea in Blood. F. Rappaport. (*Mikrochem.*, 1933–34, 14, 49–74.)—Some of the methods have been briefly described before, by the same author (*Klin. Wochenschr.*, 1932, 11, 688, and 814; *ibid.*, 1933, 12, 1184). They are suitable for the accurate determination of ammonia or urea with accuracy, in 0·1 to 0·2 ml. of serum or whole blood.

The methods are described under the following headings:—(I) Experiments on the use of the hypobromite methods for the iodimetric determination of ammonia. (II) Methods for the determination of non-protein nitrogen by distillation, (*a*) in whole blood and serum after precipitation of the protein with phosphomolybdic acid; (*b*) in whole blood and serum after precipitation of the protein with sodium tungstate; (*c*) in unhaemolysed whole blood. (III) Determination of non-protein nitrogen without distillation. (IV) Methods for the determination of urea, (*a*) in serum and whole blood, (*b*) in unhaemolysed whole blood.

(I) The *reagent solutions* for the hypobromite method are: (*a*) *Buffer solution*: 84·5 grms. of boric acid and 14·6 grms. of sodium hydroxide are dissolved in 800 ml. of water, boiled for half-an-hour to remove any ammonia, cooled and diluted to 1 litre. (*b*) A 0·1 *N* bromine solution converted into 0·01 or 0·005 *N* hypobromite solution immediately before use. The bromine solution is made up from 20 grms. of potassium bromide dissolved in water, 100 ml. of 0·1 *N* sulphuric acid, 8 grms. (2·5 ml.) of bromine, and water to 1 litre. This solution will keep for a long time in the dark. The solution may also be made by dissolving 32 grms. of potassium bromide and 2·8 grms. of potassium bromate in a little water, adding 200 ml. of *N* sulphuric acid, and diluting to 1 litre after 30 minutes; the final acidity of the solutions prepared by the two methods is the same. Before use 10 ml. of the bromine solution are mixed, with cooling, with *N* sodium hydroxide solution until the colour changes from brown to lemon yellow. Then 40 ml. of the bromate buffer solution (*a*) are added, and the mixture is diluted to 100 ml. (giving a 0·01 *N* solution, to be standardised against 0·01 *N* thiosulphate). *Method.*—For the titration, 10 ml. of the 0·01 *N* hypobromite solution are used, the test solution (such as a few ml. of *N*/300 ammonium sulphate solution) is then added, and, after a few minutes, a few crystals of potassium iodide and 2 ml. of a 15 per cent. (by weight) solution of hydrochloric acid are added, and the excess of sodium hypobromite is determined by titration with 0·01 *N* thiosulphate solution. The number of ml. of 0·01 *N* hypobromite solution used, multiplied by 0·0467, gives the number of mgrms. of nitrogen present. Excellent results for amounts varying from 0·05 mgrm. to 0·4 mgrm. of nitrogen were obtained both directly on ammonium sulphate solutions, and also after distillation in the Parnas and Wagner apparatus, but with a small wad of silver wool at the upper end of the silver condenser to trap any minute traces of sulphides that might be present. The ammonia is distilled directly into an excess of hypobromite solution.

(II) When whole blood is haemolysed with a hypertonic solution of sulphuric acid and sodium sulphate, the protein can then be precipitated with either phosphomolybdic acid or sodium tungstate, and the non-protein nitrogen values for serum and whole blood are found to agree well. The sodium sulphate solution is made up from 20 grms. of anhydrous sodium sulphate, dissolved in water, and diluted to 1 litre after the addition of 69 ml. of 2/3 *N* sulphuric acid; 5·8 ml. of this are used for each sample. The rest of the procedure is the same as the usual semi-micro method, except that the distilled ammonia is titrated as described in (I) above. Good agreement, within 1 to 2 per cent., is obtained on samples analysed by the micro- and semi-micro-methods.

(III) The nitrogen can be determined without distillation after the organic matter has been destroyed by one of two methods: (i) Where the protein is precipitated by means of phosphomolybdic acid; 2 ml. of the following reagent are used for ashing:—1 grm. of phosphomolybdic acid is dissolved in about 50 ml. of water, followed by 1 ml. of a 27 per cent. solution of sodium hydroxide, and the mixture is boiled for about 20 minutes. After cooling, 35 ml. of concentrated sulphuric acid are added, and the mixture is diluted to 100 ml. (ii) Where the protein is precipitated with sodium tungstate; 2 ml. of a suspension of 1 grm. of titanium hydroxide in 50 ml. of water and 1 ml. of Kjeldahl alkali, which has been steam-distilled until the evolving steam will no longer turn red litmus blue, are used for ashing.

When the ashing is complete, 5 ml. of a neutralising solution are added. This is made up from 3 parts of (*a*), 0·5 part of (*b*), and 1·5 part of (*c*):—(*a*) A solution of 27 grms. of sodium hydroxide in 100 ml. of water; (*b*) 15 mgrms. of methyl red dissolved in 10 ml. of *N* sodium hydroxide solution and diluted to 1000 ml.; (*c*) 10 per cent. sodium fluoride solution.

After the addition of this reagent the solution, which is still acid, is neutralised, drop by drop, with concentrated sodium hydroxide until the colour-change of brown to yellow occurs. The mixture is transferred quantitatively to a tube containing the hypobromite solution, and the titration is carried out as before. The hypobromite used in this case is about *N*/50. The results agree within about ±2 per cent. of the values obtained by the distillation method. The same hypobromite titration method is utilised for the determination of urea. There was excellent agreement between results obtained by this method and by the macro method. J. W. M.

Sensitive Reaction for Boric Acid. A. S. Komarowsky and N. S. Poluektoff. (*Mikrochem.*, 1933–4, **14**, 317–320.)—The colours of certain azo-dyestuffs in concentrated sulphuric acid are changed by boric acid. This is probably due to the formation of an inner complex compound between the dyestuff and boric acid. Azo-dyestuffs prepared from chromotropic acid (1.8-dihydroxy-naphthalene-3.6-disulphonic acid) are very suitable for this test, and especially the compound "chromotrope 2B" (*p*-nitro-benzene-azo-chromotropic acid). The test is carried out as follows: A drop of the test solution (slightly alkaline to prevent volatilisation of the boric acid) is evaporated to dryness in a porcelain micro-crucible. The residue is mixed, while warm, with one or two drops of the reagent, and the colour is observed on cooling. In the presence of boric acid the colour changes from blue-violet to greenish-blue. A blank test is required only when the amount of boric acid present is very small. The reaction is very sensitive, and enables 0·08γ boron to be detected in 0·04 ml., *i.e.* with a concentration limit of 1 : 500,000. Fluorides interfere with the test (see below). The presence of oxidising substances (nitrates, chlorates, etc.) causes decomposition when the reagent is added, and the colour changes to pink or yellow. Oxidising substances must therefore be removed as follows:—A drop of the test solution is mixed in a micro-crucible with a small amount of hydrazine sulphate, evaporated to dryness, and finally heated until fumes of sulphuric acid are evolved. The warm residue is treated with two or three drops of the reagent, and the colour observed. In this way 0·25γ of boron can be detected in the presence of 13,000 times the amount of potassium nitrate or 11,600 times the amount of potassium perchlorate.

Test for Boric Acid in the Presence of Fluorides.—In order to prevent the formation of the complex boro-fluoric acid or BF_3, the fluorine should be completely, or almost completely, removed by heating with silica in acid solution, whereby the main portion of the boric acid remains in the residue. One or two drops of the test solution are mixed with a few cgrms. of powdered silica and 1 or 2 drops of concentrated sulphuric acid, and the mixture is cautiously heated in a micro-crucible until fumes of sulphuric acid are evolved. Three or four drops of the reagent are then added and, on cooling, the colour is compared with that of a blank test. In this way 0·5γ of boron can be detected in the presence of 2300 times the amount of sodium fluoride.

Test for Boron in Minerals, Rocks, Enamels, etc.—A little of the finely-ground test powder is heated with potassium hydroxide in a silver micro-crucible. The cold melt is taken up with 5 to 6 drops of water and poured into a porcelain crucible, and one or two drops are filtered through a capillary with a piece of filter paper over the tip. The filtrate is evaporated to dryness and the test is carried out on the residue. If oxidising substances (*e.g.* chromic acid) are also present, they must first be reduced as described above.

Preparation of p-*Nitro-benzene-azo-chromotropic Acid.*—Diazotised *p*-nitraniline is coupled with chromotropic acid in solutions made alkaline with sodium hydroxide. The hydrochloric acid solution of *p*-nitraniline is diazotised at 0° C. by mixing with the calculated amount of potassium nitrite, also at 0° C. This solution is slowly mixed with the alkaline solution of chromotropic acid. The dyestuff is "salted out" with sodium chloride, filtered off, and dried on a porcelain plate. It is purified either by dissolving it in water and "salting out" again, or by taking it up in concentrated acetic acid and re-precipitating with ether. The reagent is a 0·005 per cent. solution of the dyestuff in concentrated sulphuric acid. J. W. M.

Microchemical Tests. X. L. Rosenthaler. (*Mikrochem.*, **1933–34, 14,** 268–270.)—*Alkaline Earth Sulphate Precipitation.*—The certainty of Behrens' crystalline precipitation tests depends largely on the amount and nature of other substances present, and the sensitivity may be increased or decreased. Observations were carried out on the alkaline earth sulphate test, using in each case 2·5 per cent. solutions of the alkaline earth salt.

Barium Sulphate.—Behrens and Kley (*Mikrochem. Analyse,* Vol. I, 4th Ed., p. 58) state that barium sulphate precipitated with sulphuric acid or sulphates comes out as a fine powder. Tests carried out with the acetate, chloride and nitrate of barium, precipitated with potassium sulphate, potassium bisulphate, sodium sulphate, magnesium sulphate and ammonium sulphate showed that in most cases the amorphous powder was accompanied by crystals of many shapes, mostly rod- and needle-shaped forms, in small or large aggregates. Usually the crystalline form exceeds the amorphous in amount (except with barium nitrate). The presence of sodium chloride, potassium bromide or potassium iodide causes the precipitate to be almost entirely amorphous, with the exception of barium chloride precipitated in the presence of potassium bromide by magnesium sulphate, and of barium nitrate precipitated in the presence of sodium chloride by potassium sulphate.

Strontium Sulphate.—Behrens and Kley (*loc. cit.*, p. 54) state that a finely-divided precipitate is obtained on precipitation with dilute sulphuric acid. On testing the nitrate, lactate and bromide of strontium with the same sulphates as for barium, groups of needle-shaped crystals were always formed among the amorphous precipitates; these disappear in time. The presence of bromide or iodide caused spherical crystals to be formed, whilst sodium chloride increased the amorphous precipitation.

Calcium Sulphate.—Calcium sulphate readily crystallises. Ammonium sulphate gives four-cornered plate-like crystals with oblique end-surfaces with calcium acetate, but not with the nitrate, chloride, bromide or chlorate. Potassium bisulphate gives with the above salts, spear-shaped crystals, many-sided plates and oval forms. Sodium sulphate gives small prisms. Magnesium sulphate and calcium acetate give crystals of the same shape as with ammonium sulphate. Halogen compounds have little effect on the crystal formation, but sodium chloride changes the normal form of the crystals obtained from potassium bisulphate and the acetate, nitrate and chlorate of calcium, and the same crystals are formed as from calcium salts and sodium sulphate. J. W. M.

Physical Methods, Apparatus, etc.

Some Optical and Crystallographical Properties of the Zinc Uranyl Acetates. H. Insley and F. W. Glaze. (*Bureau of Stds. J. Research*, 1934, **12**, 471–474.)—Crystals of the zinc uranyl acetates of sodium and lithium are monoclinic and isomorphous, and are capable of forming a series of solid solutions, as shown by the homogeneity, intermediate optical properties and *X*-ray pattern of a mixed sodium and lithium zinc uranyl acetate. Potassium zinc uranyl acetate, on the other hand, is tetragonal, and differs from the corresponding sodium and lithium salts in optical properties. These results are consistent with the fact that potassium can be separated from sodium by the zinc uranyl acetate method, but they indicate that there is little prospect that a satisfactory separation of sodium and lithium by precipitation with zinc uranyl acetate can be made.

S. G. C.

Reviews

CLINICAL TOXICOLOGY. By E. LESCHKE. Translated by C. P. STEWART, M.Sc., Ph.D., and O. DORRER, Ph.D. Pp. 346. London: J. & A. Churchill. 1934. Price 15s.

The publishers of this work have, during the last few years, been responsible for the production of a number of valuable works known as the "Recent Advances" series, which have been written and published in this country. The book which forms the subject of this review could, so far as size, appearance, and aim are concerned, fairly be regarded as belonging to this series, but for the fact that it is a translation of a German work.

The English edition contains not only the original text by Leschke, but a contribution from Koelsch dealing with industrial poisons. It has been found convenient by the translators to incorporate some of this in Leschke's text and to place the remainder in an appendix. There is also a short appendix by Meixner on *post-mortem* examination and the detection of poisoning.

As the title suggests, the book is primarily intended for the practising physician, and the analyst will find but little to assist in the detection and estimation of poisons. Nevertheless, a knowledge of the action of poisons is essential to those who desire to study methods of detection from a scientific standpoint.

Many of the standard textbooks of toxicology in this country, whilst dealing fully with all the classical poisons, have little or nothing to say about the effects of the rapidly increasing number of modern drugs, particularly the synthetic group. The value of the work under review lies essentially in this direction, and the accounts given of the poisonous effects of what may be called the synthetic group of drugs are thorough and fairly complete.

In this connection it may be noted that, although ample references are given at the end of each section to published work, nearly all the references are to German papers. The conclusion to be drawn from this observation and from reading the text is that, had the literature of other countries, notably France, America, and this country, been studied more fully, a very much more comprehensive account would have been forthcoming, which would have been more authoritative. It is not desired to call attention to inevitable misprints which occur in every book and which in this case are few, except to mention that confusion has apparently occurred over the name "Allonal." According to the index "Allonal" and "Allional" are distinct drugs, but on studying the references it is clear that when allional is written allonal is intended, and the reviewer has not heard of allional. Allonal is a mixture of pyramidon and isopropyl-allyl-barbituric acid. It is, perhaps, a pity too that, as many people with a limited chemical knowledge will read this book, the same compound is referred to as isopropyl-propenyl barbituric acid on page 193, as isopropyl-allyl barbituric acid on page 337, and as 5-isopropyl-5-allyl-barbituric acid on page 339.

In conclusion, reference may properly be made to the care and thoroughness which the translators have shown in the production of the English edition.

G. ROCHE LYNCH

ORGANIC SYNTHESES: AN ANNUAL PUBLICATION OF SATISFACTORY METHODS FOR THE PREPARATION OF ORGANIC CHEMICALS. Vol. XIV, pp. vii+100. Editor-in-Chief: W. W. HARTMAN. New York: John Wiley & Sons, Inc.; London: Chapman & Hall, Ltd. 1934. Price 10s 6d. net.

The fourteenth volume of this well-known series has now been issued. Twenty-six new preparations, each arranged in the usual manner, are described in detail. The substances dealt with are, for the most part, of somewhat complex structure, and are of special rather than general interest, but the teacher of advanced organic chemistry will find the preparations of *o*-bromophenol, 5-methylfurfural, nitrothiophen and 2 : 6-dimethyl-pyridine worthy of attention.

The inclusion of a preparation of glycerol α-γ-dibromohydrin may, perhaps, raise hopes in the minds of those interested in the question of the structure of glycerides, although, so far as the reviewer can see, there is no guarantee that the material described is free from isomeric bromohydrins. It is, nevertheless, a gain to be able to obtain a clean and apparently homogeneous product.

The book concludes with references to previous volumes together with additions culled from more recent sources. Several important corrections are also included. The index covers the subject matter contained in Volumes X to XIV of this series.

The present publication is quite up to the high standard of the previous issues, and thus naturally demands a place in all chemical libraries.

HAROLD TOMS

DICTIONARY OF COLOUR STANDARDS. British Colour Council, 28, Sackville Street, London, W.1. 1934. Price: £2 2s. inclusive of standard colour charts.

There are several qualities of the many material substances with which chemists have to deal that are ill to define. Readily-occurring to the mind are the two qualities of odour and colour. A scientific classification of the former quality has been attempted in a tentative way, and whilst many classifications of colours, of differing value, have been announced from time to time, few of these schemes have had any scientific foundation.

A really satisfactory scheme of colour classification would, in the writer's view, be of considerable service to analytical chemists, and there is great promise for them in the scheme now successfully launched by the British Colour Council. Mr. R. F. Wilson, the Manager and Secretary of the Colour Council, has approached the subject from the joint standpoints of an artist and a technical colour expert, and he has enlisted the assistance of many outside authorities.

This Dictionary of Colour Standards records 220 standard colours, named, numbered, and coded, the records being in the form of plain and ribbed silk-ribbon strips; and the companion volume (100 pp.) gives the reason and authority for such standardisation, and contains a list of hundreds of colour-names referring to the colours shown. As stated in the Annual Report of the British Colour Council for 1933, "the compilation should help to simplify the tasks of colour users, by reducing existing chaos in nomenclature and facilitating a more exact definition of accepted colours." The Dictionary has been adopted by the British Standards Institution as B.S.I. Standard No. 543, 1934.

The silk ribbons in the colour chart are dyed true to colour-shade, and care has been taken to ensure fastness to light. The standards will, with reasonable use, remain unchanged for a long time, but unnecessary exposure should be avoided. At any time the colours can be checked, if necessary, by comparison with the standards in the possession of the Colour Council. The scheme is sufficiently comprehensive to allow the chemist to record by name and number almost any shade of colour, whatever the nature of the coloured material. But the dictionary also records for scientific users, (i) the Lovibond Tintometer colour readings, made by Tintometer, Ltd., of Salisbury; and (ii), the colour measurements on the C.I.E. system, made by A. Hilger, Ltd., on the Guild Trichromatic Colorimeter, for each colour in the charts and dictionary, and this puts the subject at once on a scientific basis. In course of time, should this scheme find a use amongst chemists, it is understood that the Colour Council would favourably consider the preparation of charts giving colour-strips on cards, should these be considered preferable for certain purposes to the woven silk ribbons.

It is easy to visualise the many uses to which such a standard scheme of colours as that here described can be put by chemists, and the writer hopes at a later date to submit a further communication on the subject.

ARNOLD R. TANKARD

A SUMMARY OF FOOD LAWS AND REGULATIONS. By C. L. HINTON, F.I.C. Pp. 90. London: The Nema Press, Ltd., 33, Tothill Street, S.W.1. 1934. Price 21s.

Mr. C. L. Hinton, who is, of course, well known for his work on the determination of sugars as applied to foodstuffs, has attempted a survey of the world's food laws. In spite of the obvious difficulties, he has produced a very readable account, in thirteen chapters, of the similarities and diversities of the various regulations made by different States with the object of protecting the food supplies of the inhabitants. It must not necessarily be taken as additional proof of the hardiness of Britons that they are apparently allowed to consume with impunity substances that are regarded as definitely deleterious by the Governments of other nations, but is it evidence of our insular superiority that we are supposed to have sufficient intelligence to safeguard our pockets and our health by the wisdom of our purchases, whilst the Governments of other countries do not pay a similar compliment to their own peoples?

After a short introductory chapter, other chapters are given over to: milk products; sugar confectionery; cocoa and chocolate; jams; preserves and jellies; canned fruit and vegetables; canned and potted meats; pickles, sauces, etc.; non-alcoholic beverages; labelling; preservatives and colouring matters. Following this, extracts from the food legislation of the United Kingdom and the Standards for Jam of the Food Manufacturers' Federation are given, this portion being edited by Mr. T. W. Jones, the Editor of "Food." The third portion of the book consists of a series of tables giving a résumé of the standards for a large number of foods as fixed by nineteen different countries, whilst a final table gives the synthetic colours permitted in fourteen different countries.

The book gives many evidences of careful compilation and will be of considerable use to manufacturers and exporters, apart from its value in showing the great differences between the food laws of this and other countries. The binding, printing and paper are good, but the price is far too high, particularly as the book contains seventeen pages of advertisements.

G. D. ELSDON

THE BRITISH PHARMACEUTICAL CODEX, 1934. The Pharmaceutical Press. Price 35s.

The issue of a Fourth Edition of the Codex, following that of the tenth British Pharmacopoeia in 1932, gives pharmaceutical and medical practitioners the very latest information on matters pertaining to their callings, but the title-page description of the new Codex as *an Imperial Dispensatory for the use of Medical Practitioners and Pharmacists* indicates how much more comprehensive it is than the "B.P."

The need for the Codex was foreseen by the Pharmaceutical Society as far back as 1903, and the three earlier editions have been adequate testimony to the usefulness of such a book.

The Codex has established itself as a standard for many drugs and their preparations, and in the absence of any binding legal standards it is frequently accepted for purposes of evidence in courts of law, but, as it reminds us, only for substances when they are sold for use in medicine.

The new volume consists of four parts dealing with: I, General Monographs on Chemicals, Crude Drugs, etc.; II, Surgical Dressings; III, Formulary; and IV, Appendices.

Undoubtedly the monographs will be the most generally valued part of the book, for they give a description of practically everything known to, or used in, modern medicine.

Those which deal with chemicals follow closely on the lines of the Pharmacopoeia, and give the chemical formulae, and a description of the substances with a standard of purity or strength, methods of analysis or assay, and a most informative paragraph on each one's "action and uses." This is of great importance to analysts, who, however competent they may be as chemists, may know everything pertaining, say, to the chemistry of aniline, but very little regarding the clinical manifestations of poisoning by aniline or the medicinal action of some of its derivatives. This section of the monographs has been prepared with the assistance of pharmacologists of eminence, and the co-operation of chemists and medical men has resulted in a large amount of really valuable and helpful information.

The monographs dealing with crude drugs and plants are exceptionally well compiled; the botanical sources of all the known important drugs given are in agreement with most recent information, and the descriptions of the diagnostic microscopical characters of the powdered drugs should make the Codex a reference book for all who have to deal with pharmacognosy and plant histology.

Peppermint, sage and thyme are seldom used, as such, in medicine, but the Codex gives limits for ash or acid-insoluble ash and foreign organic matter, which are useful guides to purity.

The limit for the amount of volatile oils is specified for sage and thyme, and, together with those for some of the drugs, show that a determination of this important constituent of drugs and herbs may be needed in future. Peppermint is said to "contain volatile oil," and so is spearmint, but nothing is mentioned about adulterants or microscopical characters of the leaf, which should be of more significance than the description of the flowers, as these are seldom present in the rubbed herbs.

Such important substances as oestrin, parathyroid, thyroid gland, pituitary, and suprarenal gland are dealt with very fully, and insulin is described most helpfully. Under Yeast and Irradiated Ergosterol, most of the modern vitamin information is made available, but the paragraphs on Diastase and Extract of Malt are somewhat condensed, possibly owing to their altered position in therapeutics.

The Antitoxins and Toxins are dealt with in much the same way as in the B.P., but all the information is of extreme importance to the modern physician.

Part II, dealing with Surgical Dressings, is the first published description of any significance in this realm of medical treatment, but how important they are will be acknowledged when the quantities produced for the hospitals and National Health Insurance work are taken into account. The Latin names adopted for the homely bandage, gauze, and muslin may seem unnecessary, but evidently meet some medical requirement, although the public would need something more than "Ligamentum Textum Apertum" with which to be blindfolded to-day.

Probably Part III of the Codex will come before the notice of Public Analysts more than any part of the book, for it consists of formularies for preparations of the drugs and chemicals in use for medicine and for sale to the public to-day. There are so many things bought and sold for which there is no standard of strength or purity that these formularies will be accepted in many cases as reasonable.

Emulsion of Cod-liver Oil is ordered to be made to contain 10 fluid ounces of the oil in 20 fluid ounces of the product. There may be other long-standing recipes for it, but here is a proposed standard of strength.

If standards were proposed for such things as mustard and ground almonds in the Codex, they could only apply when those substances were to be used for medicinal purposes, just as borax, not free from arsenic, cannot, or does not, come within the range of the B.P. limits of purity if it is used for laundry work.

In the large number of formulae contained in the 370 pages devoted to them, there are some which will need further consideration, but that is not the fault of the committees responsible for their inclusion.

A number of appendices are included, as is customary in such books, but the tables for Dilution of Alcohol will be useful, and the sections dealing with Determination of Foreign Organic Matter in Powdered Drugs, Hydrogen Ion Concentration, and Sterilisation make most useful chapters of reference on modern methods.

"Substances with Proprietary Trade Names" is a most important addition for both pharmaceutical and medical reference, and will be used as frequently as any part of the book by many workers.

The successful compilation of such a book by a number of voluntary committees is evidence both of the enthusiasm of the members, all of whom are specialists in their own sphere of work, and of their recognition of the value of good team-work, but a special tribute is due to the editor who was able to co-ordinate such a mass of information in an intelligible work of reference, which will be used by chemists, pharmacists, and the medical profession generally the whole world over.

C. EDWARD SAGE

Publications Received

A MANUAL OF BIOCHEMISTRY. By J. F. McCLENDON. London: Chapman & Hall, Ltd. Price 31s. net.

DUST. By S. C. BLACKTIN. London: Chapman & Hall, Ltd. Price 18s. net.

VOLUMETRIC ANALYSIS. By H. P. STARCK. London: Baillière, Tindall & Cox. Price 7s. 6d.

ANCIENT EGYPTIAN MATERIALS AND INDUSTRIES. By A. LUCAS. Second Edition, Revised. London: Edward Arnold & Co. Price 16s. net.

THE BUCHEUM. By Sir ROBERT MOND and O. H. MYERS. WITH THE HIEROGLYPHIC INSCRIPTIONS, edited by H. W. FAIRMAN. Forty-first Excavation Memoir. Three Vols. London: Egypt Exploration Society. Price 50s.

A SCHEME FOR THE DETECTION OF THE MORE COMMON CLASSES OF CARBON COMPOUNDS. By F. E. WESTON. London: Longmans, Green & Co. Price 4s. 6d.

"ANALAR" STANDARDS FOR LABORATORY CHEMICALS. With a foreword by Professor J. F. THORPE. London: The British Drug Houses, Ltd., and Hopkin & Williams, Ltd.

PRACTICAL BACTERIOLOGY: AN INTRODUCTORY COURSE FOR STUDENTS OF AGRICULTURE. By ANDREW CUNNINGHAM. London: Oliver & Boyd.

PHOTOGRAPHY AS AN AID TO SCIENTIFIC WORK. [A list of photographic materials suitable for astronomy, biological sciences, chemistry and physics, geology, medicine and radiography, and metallurgy.] Ilford: Ilford, Ltd.

WATER STERILISATION. Imperial Chemical Industries, Ltd. Pp. 50. [Introduction—Water sterilisation by gaseous chlorine—Simple chlorination—Superchlorination and dechlorination—Ammonia—Chlorine treatment—Relative merits of methods—Industrial applications—Determination of free chlorine in water—Bibliography.]

SANDS, CLAYS AND MINERALS. Vol. II. August, 1934. Published by A. L. Curtis, Chatteris. Price 3s. 6d., post free.

A PRACTICAL CHEMISTRY FOR HIGHER SCHOOL CERTIFICATES AND INTERMEDIATE STUDENTS. By G. P. McHUGH. Pp. viii + 117. London: Longmans, Green & Co., Ltd. 1934. Price 2s. 9d.

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THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

An Ordinary Meeting of the Society was held at the Chemical Society's Rooms, Burlington House, on Wednesday, October 3rd, the President, Mr. John Evans, M.Sc., F.I.C., being in the chair.

Certificates were read in favour of:—Victor Cecil Branson, A.R.C.Sc., D.I.C., B.Sc., A.I.C., Roydon George Cowdell, Joseph Davies, F.I.C., Frank Akerman Hatch, A.I.C., Herbert Lloyd Hind, B.Sc., F.I.C., Alexander Marr, A.M.C.T., Daniel Donald Moir, M.Sc., F.I.C., Teunis Potjewijd, D.Sc., Magnus A. Pike, B.Sc., Walter James Rees, M.Sc., F.I.C., James Sandilands, F.I.C., William Wilders Taylor, B.Sc., F.I.C., William Pearson Thistlethwaite, B.Sc., Frederick Thomas, M.Sc., Dennis Gordon Tompkins, B.Sc., A.I.C.

The following were elected Members of the Society:—John Ferguson Brown, B.Sc., A.I.C., Carl Emil Resch, B.Sc., Wilfred Smith, B.Sc., A.I.C., Sidney George Edward Stevens, B.Sc., A.I.C.

The following papers were read and discussed:—"The Determination of Lead in Biological Material, with Special Reference to Bone," by G. Roche Lynch, O.B.E., M.B., B.Sc., D.P.H., F.I.C., R. H. Slater, D.Sc., Ph.D., F.R.S.E., A.I.C., and T. G. Osler, M.B., Ch.B., M.R.C.S., L.R.C.P.; "The Determination of 'Ethyl' Vanillin," by H. C. Lockwood, B.Sc., A.I.C.; and "The Detection and Identification of Metallic Particles in Manufactured Products," by H. C. Lockwood, B.Sc., A.I.C.

NORTH OF ENGLAND SECTION

A meeting of the Section was held in Manchester on October 13th. The Chairman (Professor W. H. Roberts) presided over an attendance of thirty-five.

The following papers were read and discussed:—"The Composition of the Amniotic Fluid," by Arnold R. Tankard, F.I.C., D. J. T. Bagnall, F.I.C., and F. Morris, F.I.C.; "A Note on the Dictionary of Colour Standards of the British Colour Council," by Arnold R. Tankard, F.I.C.; and "Mrs. Beeton, the Housewife and the Factory," by E. Hinks, B.Sc., F.I.C.

Standards for Purity and the Determination of "Ethyl" Vanillin

By H. C. LOCKWOOD, B.Sc., A.I.C.

(*Read at the Meeting, October* 3, 1934)

VANILLIN and its homologue, *m*-ethoxy-*p*-hydroxybenzaldehyde, are very similar in chemical reactions. The flavour of "ethyl" vanillin is four or five times as strong as that of ordinary vanillin, and it is claimed that it resembles more closely that of vanilla, the natural product. Since the price of "ethyl" vanillin is about two and a quarter times that of vanillin, it was considered possible that adulteration might occur. To detect this, the reactions of the two substances were studied to see if it were possible to obtain a characteristic divergence. Most of the tests give identical qualitative reactions, but the following method was devised and found to be satisfactory.

BROMINE TEST.—Two grms. of "ethyl" vanillin are mixed with 5 ml. of cold water in a small beaker and allowed to soak for 15 minutes. The mixture is then filtered through a 5·5 cm. filter paper, and 1·7 ml. of the filtrate is collected in a dry 10-ml. graduated measure. The filtration is aided by pressing the mixture into the filter paper with a glass rod. The solution should give a slightly acid reaction with litmus paper. The measured volume of the filtrate is then diluted to 5 ml., giving a one-third saturated solution. To this is added 0·5 ml. of saturated bromine water.

If the "ethyl" vanillin is free from vanillin, the solution is at first yellow or orange changing to yellow, with no precipitation or cloudiness, whilst in the presence of vanillin a red colour is first formed, and finally a red-brown precipitate. The test is capable of detecting the addition of 0·5 per cent. of vanillin to "ethyl" vanillin.

The test depends for its success on the difference in solubilities of vanillin and "ethyl" vanillin, the cold saturated solutions containing 0·8 and 0·4 per cent., respectively.

Some other chemical impurities which may possibly be present, such as piperonal, are capable of producing a cloudiness, but not the red colour caused by the presence of vanillin.

MELTING-POINT.—Vanillin and "ethyl" vanillin melt at 82° and 77° C., respectively. On mixing, a eutectic point is reached at about 50° C., when the mixture contains 40 per cent. of vanillin and 60 per cent. of "ethyl" vanillin. A mixture of 90 per cent. of vanillin and 10 per cent. of "ethyl" vanillin, after fusing together and solidifying, melts at 77° C., so that only this proportion could hope to pass as pure "ethyl" vanillin, and the bromine test would then detect the adulteration.

DETERMINATION OF "ETHYL" VANILLIN.—It was found that, although vanillin and "ethyl" vanillin reacted in a similar way, there were differences of sufficient magnitude to render the usual methods for the former unreliable for the latter. The following processes were tried:

(*a*) The semicarbazide precipitation method of Phillips (ANALYST, 1923, **48**, 367), which gives satisfactory results with vanillin, was tried, but low results were obtained. This was due to the higher solubility of the "ethyl" vanillin semicarbazones which is, according to the figures below, about six times as soluble as the vanillin compound. Saturated aqueous solutions of the semicarbazones were prepared at 15·5° C. and found to contain the following amounts:

Vanillin semicarbazone	6 mgrms. per 100 ml.
"Ethyl" vanillin semicarbazone	35 „ „ 100 „

The solubility of "ethyl" vanillin semicarbazone in the reaction mixture was also studied and found to be 27 mgrms.

(*b*) The *p*-toluidine method gave fairly good results if the precipitate was not dried above 50° C. The objection was that a constant weight was not reached, owing to the volatile nature of the precipitate.

(*c*) The 1929 Annual Report of Schimmel & Co. (p. 123) contains a titrimetric method in which thymol-phthalein is used as an indicator. The end-point is very indefinite, which reduces the accuracy of the process.

(*d*) Palfray, Sabetay, and Soutag (*Compt. rend.*, 1932, **194**, 1502; Abs. ANALYST, 1932, **57**, 472) give a method for aromatic aldehydes based on Cannizzaro's and Claisen's reactions, using potassium hydroxide in benzyl alcohol. After refluxing, the alcohol was very dark brown owing to decomposition, and it was impossible to titrate it.

(*e*) A method based on iodine absorption was tried, but without success.

(*f*) Zeisel's reaction for methoxy and ethoxy groups gave low results with pure specimens:—Vanillin gave 97·9 and "ethyl" vanillin 95·5 per cent. It is generally accepted that compounds containing ethoxy groups give low results by this method, which is also too tedious for control analysis.

(*g*) A process based on bromine absorption was devised, and, after a suitable sealing material for the stoppers had been found, it gave duplicate results which agreed closely. Of the various substances tested to prevent loss of bromine through the stoppers, orthophosphoric acid was found to be the most effective. Bromine was found to be insoluble in the acid and also without action upon it.

BROMINE ABSORPTION METHOD.—The following solutions are required:—

(*a*) Bromine solution (2·5 per cent.) is prepared by dissolving 0·82 ml. of bromine in each 100 ml. of glacial acetic acid. The solution keeps well in the dark.

(*b*) Sodium thiosulphate (5/32 *N*). Dissolve 38·78 grms. of pure sodium thiosulphate ($Na_2S_2O_3.5H_2O$) in water and make up to 1 litre.

One ml. of 5/32 *N* sodium thiosulphate is equivalent to

0·0125 grm. of bromine
or 0·01188 „ „ vanillin
or 0·01297 „ „ "ethyl" vanillin.

(*c*) Each determination and blank requires a thin glass phial containing 3 grms. of potassium iodide dissolved in 3 ml. of water, which gives a volume of 4 ml. The glass phials are conveniently blown to ½-inch diameter from ¼-inch tubing, and, after introduction of the potassium iodide solution, they are sealed. The tubes should be washed and prepared just before use, as potassium iodide solution liberates iodine on keeping.

The "ethyl" vanillin (0·5 grm.) is weighed to 0·1 mgrm. in a small tube. The tube is introduced into a stoppered stout glass bottle of 400 to 600 ml. capacity, containing a phial of potassium iodide solution. The tube is conveniently slid down a cylinder of paper inside the neck of the bottle. The contents of the tube are shaken out by bumping and rotating the bottle, since, if left in the narrow tube, the substance dissolves with difficulty.

The bromine is added by means of a 50-ml. pipette fitted with a cork and side-tube, so that it can be filled by pressure. The pipette is filled once with the solution and allowed to empty before use. Fifty ml. are pipetted for the determination and the blank test. The stopper is then smeared with syrupy orthophosphoric acid of sp.gr. 1·73. When the "ethyl" vanillin has dissolved, the bottles are placed in the dark and rotated after the first hour. At the end of six hours each bottle is shaken vertically, so that the glass phial is broken by hitting the top or bottom, since there is a distinct possibility of breaking the absorption bottle if the phial strikes the side. The liberated iodine is titrated with 5/32 *N* thiosulphate solution. This is conveniently done by adding 50 ml. of 5/32 *N* thiosulphate solution to each bottle from a pipette, counting the same number of drops, and continuing the titration from a burette, or using a 100-ml. burette having a bulb for the first 50 ml. Towards the end of the titration starch solution is added, and the end-point is given to one drop.

The blank should require 92 to 97 ml., and 0·5 grm. of pure "ethyl" vanillin accounts for 38·55 ml. 5/32 *N* thiosulphate solution. From the difference between the blank and test solution is calculated the purity of the "ethyl" vanillin. The titrations must be carried out with the greatest accuracy, since 0·1 ml. of 5/32 *N* thiosulphate solution is equivalent to 0·26 per cent. of "ethyl" vanillin when using 0·5 grm.

Two sets of results in triplicate were as follows:

1.	99·9	99·9	100·0 per cent.
2.	100·0	100·2	100·0 ,,

By this method vanillin gives results accurate to about 1 per cent.

The monobromo derivatives of vanillin and "ethyl" vanillin have melting points of 162° and 140° C., respectively.

I am indebted to Messrs. Cadbury Brothers, Ltd., for permission to publish these methods, which were investigated in their laboratories at Bournville.

Rapid Determination of Nitrogen by a Kjeldahl-Nessler Process

By W. H. KITTO, B.Sc.

THE range of work in some of the small-staffed official laboratories in the colonies is very wide, and when engaged upon major forensic problems an officer is frequently called upon to give a quick decision, *e.g.* as to whether a sample of condensed milk is a "whole-milk" product, whether a sample of human milk is of approximately average composition, whether bread advertised as specially prepared for diabetics is suitable, and so on. In connection with such samples there is need of a method for rapidly determining nitrogen with a degree of accuracy which, whilst not necessarily as great as that of the usual Kjeldahl process, would be sufficient for the purposes indicated.

Experiments were therefore made with the object of finding some method of Kjeldahl oxidation which, although much faster than the standard procedure, would yield an extract suitable for the determination of nitrogen by direct nesslerisation.

A catalyst oxidiser recommended had the percentage composition:—anhydrous sodium sulphate, 90; mercuric sulphate, 7; copper sulphate, 1·5; precipitated selenium, 1·5 per cent. It is used in quantities of 10 grms. of the mixture with 1·75 grm. of sample (of cereal meal) and 20 ml. of sulphuric acid.

This mixture (and a similar mixture in which the selenium was replaced by an equivalent amount of sodium selenate) was found to work excellently; extracts from the above quantities were clear after about 25 minutes, but were heated for 50 minutes, and, after the usual distillation, gave results which agreed well with those obtained by standard procedure.

Attempts to nesslerise these extracts, however, failed, owing to heavy precipitation, and it appeared probable that this difficulty would be encountered whenever mercury was employed as catalyst.

It was therefore decided to try the mixture recommended by Chiles (*J. Amer. Chem. Soc.*, 1928, **50**, 217) for colorimetric Kjeldahl determinations (concentrated sulphuric acid, 70 ml.; water, 50 ml.; 20 per cent. perchloric acid, 20 ml.; anhydrous sodium sulphate, 15 grms.; copper sulphate, 1 grm.). Thirty-five ml. of this mixture were taken with 1·75 grm. of a bread sample. Oxidation was slow, and the results on distillation were appreciably lower than those given by the standard procedure. It was found, however, that the results obtained by nesslerisation of the extract after appropriate dilution agreed satisfactorily with those obtained by distillation.

It was decided to try the effect of adding selenium to Chiles's mixture. As only sodium selenate was available, this was employed in the proportion of 1·15 grm. to each 100 ml. of Chiles's mixture. The result was a very marked acceleration of the oxidation.

Wheat flour (1·75 grm.) digested with 35 ml. of Chiles's mixture became clear in 45 minutes, and distillation, after 1¼ hours' total heating, gave a result which agreed well with the true value. Moreover, nesslerisation, after appropriate dilution of this digest, gave very satisfactory results.

In order to expedite nesslerisation over a considerable range, without the trouble involved in making up fresh standard solutions on each occasion, use was made of the Hellige comparator, in which the colours of nesslerised solutions in standard troughs may be matched against permanent standard shades mounted in groups of 9 on rotating discs.

It was found very desirable to standardise these discs with ammonia solutions, and from the results of duplicate standardisation with solutions of ammonium chloride and sulphate a curve was obtained from which a table was prepared giving the ammonia-content, in mgrms. per 100 ml. for any observed or estimated Hellige reading up to a maximum of 1·3 mgrm. per 100 ml. For all concentrations of ammonia above 0·4 mgrm. per 100 ml. it was found advisable to add 4 ml. of Nessler's solution per 100 ml. instead of the 2 ml. used at lower concentrations; this was done in the standardisations of the discs and in subsequent comparisons.

TESTS OF THE METHOD WITH VARIOUS SUBSTANCES.—Quantities of 0·2 to 0·5 grm. of the substances given below were oxidised in 100-ml. Kjeldahl flasks, and, after neutralisation (see below) and dilution, were nesslerised at three different strengths, and the ammonia-contents were estimated by Hellige comparator readings.

There was satisfactory agreement between the ammonia-contents deduced from readings at the different strengths, and the average nitrogen-contents deduced therefrom agreed satisfactorily with those obtained by the standard Kjeldahl procedure. The actual figures obtained were:

	Nitrogen	
	Ordinary Kjeldahl method Per Cent.	Proposed method Per Cent.
Wheat flour	1·68	1·75
Special bread	2·31	2·32
Barley "A"	1·37	1·32
Barley "B"	1·72	1·65

The method also gave satisfactory results with milk, and it was found that 2 ml. of a well-mixed sample, measured with an Ostwald pipette, was a convenient amount with which to work.

In nearly all cases the nesslerised solutions were perfectly clear, but, with some at the higher concentrations, there was a suggestion of opalescence which did not, however, affect the shades or interfere with the readings through the 4-cm. trough, or appear to prevent the concordance of the results obtained.

Nesslerising at three different concentrations was adopted with a view to eliminating any small errors associated with the colorimetric assessment by means of the discs. Blank determinations with the reagents proved that they did not interfere.

DETAILED DIRECTIONS FOR PROCEDURE.—The conversion reagent consists of Chiles's mixture (*vide supra*), to which powdered sodium selenate is added in the proportion of 1·15 grm. per 100 ml.

As there is a tendency for some of the components to separate out, this mixture should always be well shaken before use.

A quantity of 0·5 grm. of a solid substance (such as wheat flour), of 2 ml. of a liquid such as milk, or diluted condensed milk, is introduced into a 100-ml. Kjeldahl flask, together with two small glass beads, and 12·5 ml. of the conversion reagent. The flask is heated gently, with shaking, for the first five minutes, and the heating then continued in the usual way. If *t* is the time taken to clear (which is usually about 20 minutes), heat for a total period of 1·75 *t*. Cool, and wash into a 250-ml. flask, and adjust to the mark. Take 10 ml. of this diluted solution, add phenolphthalein, and titrate with *N* sodium hydroxide solution (using a graduated 10-ml. pipette). Let the amount of alkali required be *s* ml. Now transfer 40 ml. from the 250-ml. flask, to a 100-ml. flask, add (4 *s*–1) ml. of N sodium hydroxide solution, to produce a faintly acid reaction, and adjust to the mark. Take 20 ml. of this mixture and nesslerise, using 4 ml. of Nessler's reagent and diluting to 100 ml. If the depth of colour is moderate, nesslerise two other quantities of 10 ml. and 30 ml., respectively, using 2 ml. and 4 ml. of Nessler's reagent, respectively, and making up to 100 ml. If with 20 ml. the colour obtained is deep, take two smaller quantities; and if it is unduly pale, take two larger ones for nesslerisation, using 2 ml. of Nessler's reagent for the lower and 4 ml. for the higher concentrations. The ammonia-contents of the nesslerised solutions are then determined in the 4-cm. trough of the Hellige comparator by comparison with the standardised discs.

Although the detailed directions may suggest that the procedure is complicated and lengthy, the actual operations are simple and rapid; apart from the pause of 10 minutes for the development of the Nessler colours, the dilution, neutralisation, nesslerisation, and comparator measurements take only a few minutes.

It is not suggested that the above procedure will be universally applicable without modification. The use of a stabiliser, such as gum arabic as recommended by Chiles (*loc. cit.*), may be advisable in some cases, and, in the presence of appreciable amounts of the alkaline earths, the addition of Rochelle salt might be beneficial in the nesslerisation.

I wish to acknowledge the assistance given to me by Mr. A. W. Facer, B.A., F.I.C., in connection with this investigation.

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The Determination of Vanadium with Potassium Iodate, with Notes on Chloramine-T as an Oxidising Agent

By A. J. BERRY, M.A.

The analytical chemistry of vanadium is much concerned with the various states of oxidation of that element. Thus it is well known that the more powerful oxidising agents, such as potassium permanganate, can effect quantitative transformation of any of the lower stages into the quinquevalent condition. Reduction from the quinquevalent to the quadrivalent condition can be effected by the milder reducing agents, such as ferrous sulphate and sulphur dioxide. With liquid amalgams, either the bivalent or the quadrivalent stage may be realised, according as zinc amalgam (Nakazono, *J. Jap. Chem. Soc.*, 1921, **42**, 751) or bismuth amalgam (Someya, *Z. anorg. Chem.*, 1924, **138**, 291) is employed as the reducing agent. Someya has also shown that when vanadium salts are reduced to the bivalent condition in the presence of a small quantity of a dyestuff such as phenosafranine in acid solution, the latter is also reduced to the leuco compound. When the resulting solution is titrated with a suitable oxidising agent, the dyestuff is reconverted into the coloured form at the stage when quantitative transformation of the vanadium from the (violet) bivalent form into the (green) tervalent state has been effected (*Z. anorg. Chem.*, 1928, **169**, 293).

Very little, if indeed any, work has hitherto been done on the direct titration of vanadium salts with potassium iodate. As is well known, this reagent, when used in the presence of a high concentration of hydrochloric acid, can effect the quantitative oxidation of a number of substances (Andrews, *J. Amer. Chem. Soc.*, 1903, **25**, 756). Thus thallous salts may be determined by direct titration with potassium iodate (Berry, ANALYST, 1926, **51**, 137). Another method of using potassium iodate in volumetric analysis, which may be considered as a modification of Andrews' procedure, has been described in a series of publications by Lang (*Z. anorg. Chem.*, 1922, **122**, 332, and subsequently). In Lang's method the oxidation is effected in the presence of hydrocyanic acid, the iodine being oxidised to a colourless solution of iodine cyanide:

$$I\overset{\prime}{O}_3 + 2\overset{\prime}{I} + 3HCN + 3\overset{\bullet}{H} = 3ICN + 3H_2O.$$

It has been claimed by Lang and others that the "iodine cyanide" method is preferable to Andrews' "iodine monochloride" method, because (*a*) a very much lower concentration of hydrochloric acid is required, and (*b*) the end-point of the reaction can be recognised with the aid of starch, instead of using an organic solvent such as chloroform. Against this, however, it must be urged that in some titrations the end-point is less easy to recognise, and also that the evolution of the vapour of hydrocyanic acid is highly objectionable. For many purposes the two methods may be regarded as equally applicable, but such is not the case with vanadium salts. In the experiments to be described in this paper it will be seen that bivalent vanadium can be oxidised exactly to the tervalent condition by Lang's method, whereas, when Andrews' method is used, there is a slow further oxidation to the quadrivalent condition, the reaction being ill-suited to volumetric analysis. These experiments have also shown that oxidation of vanadium from the bivalent to the tervalent stage is effected with greater accuracy by Lang's method than with ferric sulphate, with phenosafranine as indicator.

Solutions of vanadic acid were readily prepared for this work by dissolving ammonium metavanadate (10 grms.) in aqueous sodium hydroxide solution, adding excess of dilute sulphuric acid, and then diluting the resulting solution with water to the desired volume (one litre). Solutions of vanadyl sulphate were prepared from this by reduction with sulphur dioxide. Those of vanadous sulphate were prepared, sometimes from vanadyl sulphate, and at other times directly from vanadic acid by the reducing action of zinc amalgam. A large number of analyses were made, of which the following may be quoted to illustrate the more interesting results. The following solutions were used:

> Potassium iodate, 3·82 grms. per litre; potassium iodide, 17·5 grms. per litre; hydrochloric acid, about 10 per cent.; potassium cyanide, 5 per cent. Fresh starch solutions were prepared for each day's work.
>
> Ten ml. of potassium iodide with 25 ml. of hydrochloric acid and 25 ml. of potassium cyanide required 29·6 ml. of potassium iodate.
>
> Twenty ml. of vanadyl sulphate were reduced to vanadous sulphate, and at once added to this colourless solution of iodine cyanide. The volume of potassium iodate required was 24·4 ml. This effected the oxidation V^{II} to V^{III}.

When similar experiments were made by Andrews' method, in which 50 ml. of concentrated hydrochloric acid were used, and, of course, no potassium cyanide was present, 10 ml. of potassium iodide required 29·6 ml. of potassium iodate as before, but, on adding the vanadous sulphate to the solution of iodine monochloride, the volume of potassium iodate required was nearly double that formerly needed. Oxidation, however, took place slowly, and the end-point was difficult to attain. It was evident, however, that oxidation had gone to the quadrivalent stage, since the consumption of the oxidising agent was twice as much as before. Moreover, the green colour of the solution at the conclusion of the reaction was identical with that of a mixture of vanadyl sulphate and hydrochloric acid containing iodine monochloride.

By way of comparison with the iodine cyanide experiments, the consumption of available oxygen over an equal but different range, *viz.* from V^{IV} to V^{V}, was found by titrating 20 ml. of the above solution of vanadyl sulphate with a solution of potassium permanganate (3·13 grms. per litre). The volume required was 17·4 ml. It follows that 24·4 × 3·82 grms. of potassium iodate, when used in a Lang titration, are equivalent in oxidising power to 17·4 × 3·13 grms. of potassium permanganate. When these products are divided by the corresponding equivalent weights, the ratios are 1·74 and 1·72, respectively. The accuracy of the iodine cyanide method for effecting quantitative oxidation from the bivalent to the tervalent condition is therefore justified.

Some experiments were made on the oxidation of vanadous sulphate with ferric alum, the end-point being determined with phenosafranine (*cf.* Someya, *loc. cit.*). In all cases oxidation to the tervalent condition was not quantitative but lower, usually about 5 per cent., even when great care was taken to avoid atmospheric oxidation of the vanadous salt. When vanadous sulphate was oxidised in this way with vanadic acid, the end-point of the reaction was found to correspond with a ratio of five parts of V^{II} to four parts of V^{V}, which does not agree with the formation of any simple compound.

In connection with this work, some experiments were made with chloramine-T as the titrant. This compound, the sodium derivative of parachlorotoluene sulphochloramide, was first introduced for volumetric work as a substitute for iodine by Noll (*Chem.-Ztg.*, 1924, **48**, 845). It was found that chloramine-T could be used instead of potassium iodate for the direct titration of potassium iodide to iodine monochloride or to iodine cyanide. As an example, the following results may be quoted:

A solution containing 18·66 grms. of chloramine-T per litre was prepared. Twenty ml. of this solution, treated with excess of acidified potassium iodide, required 25·7 ml. of sodium thiosulphate solution (15·98 grms. per litre). The value for the equivalent weight was 143·6.

Twenty ml. of a solution of potassium iodide (17·5 grms. per litre), acidified with 50 ml. of concentrated hydrochloric acid, required 32·5 ml. of chloramine-T. When dilute hydrochloric acid and 25 ml. of 5 per cent. potassium cyanide were used instead of the concentrated acid, the same volume of chloramine-T was required. The value for the equivalent weight was found to be 287·6. It is clear that the equivalent weight of chloramine-T should, when used in an Andrews or a Lang titration, be double that when used in conjunction with excess of acidified potassium iodide where oxidation does not proceed beyond the quantitative liberation of iodine.

Chloramine-T has much to recommend it as a volumetric oxidising agent. Its high equivalent weight, ready solubility, and moderate stability in solution are worthy of note. When kept in bottles of blue glass, the freshly prepared solution was found to lose about 2 per cent. of its oxidising power in the course of a fortnight at the ordinary temperature. In this respect it is decidedly inferior to potassium iodate.

In conclusion, a few words may be added with regard to the oxidation of thallous salts. Potassium iodate is, in my experience, the best reagent for this purpose, and it must be used according to the Andrews procedure. Iodine cyanide cannot be used for the determination of thallous salts, the end-point with starch being entirely unsatisfactory. On the other hand, thallous salts may be determined with accuracy by oxidation with iodine monochloride, followed by oxidation of the iodine by direct titration with chloramine-T in presence of a high concentration of hydrochloric acid. Identical results were also obtained when the thallous salts were oxidised in the presence of dilute hydrochloric acid and excess of potassium bromide by direct titration with chloramine-T, the end-point of the reaction being obtained with methyl orange as in Györy's well-known potassium bromate method for the determination of antimony.

SUMMARY.—Vanadium can be determined volumetrically by oxidation from the V^{II} to the V^{III} condition by the iodine cyanide method. The consumption of available oxygen for this range has been checked by oxidising solutions of the same vanadium-content from the V^{IV} to the V^{V} condition with potassium permanganate.

Chloramine-T can be employed in conjunction with potassium iodide, instead of potassium iodate, for the direct titration of various oxidisable substances. In particular, thallous salts can be determined by the iodine monochloride method; the iodine cyanide method cannot, however, be used. Thallous salts can also be determined by titration with chloramine-T, the reagent being used in presence of dilute hydrochloric acid and potassium bromide.

Examples of these results are appended in the following table:—

Substance Analysed (Concentration as prepared for experiment)	Oxidising Agent and method of use	Concentration as determined by analysis
10·0 grms. of NH_4VO_3 per litre.	Iodine cyanide (V^{II} to V^{III}).	10·2 grms. per litre.
Ditto.	Potassium permanganate (V^{IV} to V^{V}).	10·1 grms. per litre.
10·0 grms. of TlOH per litre.	Iodine monochloride with chloramine-T.	9·91 grms. per litre.
Ditto.	Chloramine-T used with hydrochloric acid and potassium bromide.	9·98 grms. per litre.

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The Determination of Carbon in Rocks and Minerals

BY B. E. DIXON, M.Sc., A.I.C.

CARBON occurs in rocks in a great variety of forms and to a considerably varying extent. The occurrence, in rocks, of carbon minerals or carbonaceous matter, except when these happened to be of economic importance, does not appear to have received much attention, and it is in any case difficult to determine the nature of these minerals by inspection. It is, therefore, desirable to employ for their analysis a method as widely applicable as possible. The use of the dry combustion method for this purpose has some drawbacks:—(i) When the amount of carbon is small in comparison with that of carbonate it is difficult to determine the carbon accurately by the difference of results obtained by two dissimilar methods, *viz.* total carbon by dry combustion, carbonate by treatment with dilute acids; (ii) if the combustion is complete no carbon must be retained in the ash. This is usually ensured, in the case of siliceous rocks and minerals, by fusion with lead chromate, or with a mixture of lead chromate and potassium chromate.

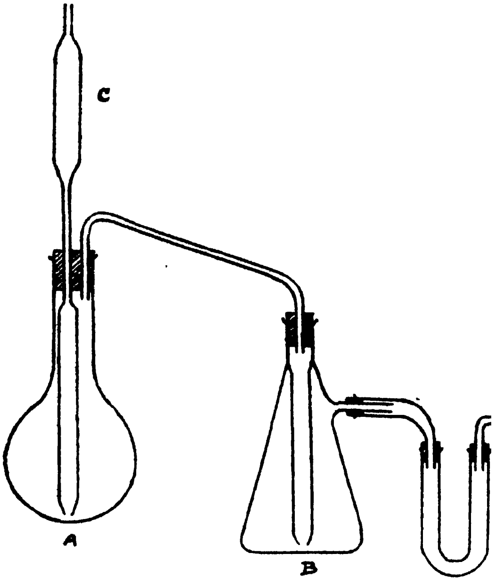
Highly refractory carbonates present a difficulty. It is impracticable to expel all the carbon dioxide by heating the sample alone in a glass tube. Admixture with lead and potassium chromates also fails to decompose the carbonates completely, and the use of potassium dichromate alone, which yields a more complete melt, is precluded by the large amount of spattering which occurs. Other objections are mentioned by Florentin (*Chim. et Ind.*, 1924, **11**, 875) and Schollenberger (*J. Ind. Eng. Chem.*, 1916, **8**, 1126).

WET COMBUSTION METHODS.—Many wet combustion processes involving the use of sulphuric and chromic acids with various catalysts have been devised for the determination of carbon in soils, graphites, coals, etc. (*e.g.* Simon, *Compt. rend.*, 1923, **176**, 1409; **177**, 122; Florentin, *Bull. Soc. Chim.*, 1924, **35**, 228). Morgan (*J. Chem. Soc.*, 1904, **85**, 1004) obtained accurate results with mixtures of calcite and definite organic substances, and with precipitated carbon from iron, by first decomposing the carbonate with phosphoric acid, then adding chromic acid, and again heating to oxidise the carbon. Morgan's method has the advantages (i) that by using phosphoric acid instead of sulphuric acid, which has itself an oxidising effect, the two forms of carbon are determined by consecutive operations in the same apparatus, and (ii) the risk of absorption of acid fumes is eliminated. Schollenberger (*loc. cit.*) stated that phosphoric and chromic acids would not completely oxidise carbon in soils unless some sulphuric acid were also present.

Since the use of phosphoric acid for the purpose in hand seemed to be more promising than that of sulphuric acid, the carbon in a number of rocks and of carbon minerals often associated with rocks was determined by Morgan's method (Table, Columns 2 and 4). The results showed that, (i) as in the case of the simple sulphuric-chromic process, low results were obtained with some samples, owing to incomplete combustion to carbon dioxide, and (ii) in all cases, provided the temperature of the flask was high enough, no carbon remained in the flask after the operation, the whole being completely expelled as carbon dioxide or other volatile substance. This was evident from inspection of the residue and from later tests (Column 3).

Attempts were made, without success, to render the combustion complete by the addition of catalysts. Apart from the fact that this did not eliminate the source of error (*a*), p. 742, the fundamental difficulty appeared to be that once the not fully oxidised products of a resistant compound had escaped from the surface of the liquid, they were immune from further oxidising action. There remained, therefore, no alternative to the provision of a further oxidising medium to complete the combustion. A solution was found in the insertion of a second flask provided with a wide inlet-tube and containing phosphoric and chromic acids together with a little mercuric oxide. This flask served the two-fold purpose of acting as a condenser to trap volatile constituents expelled during the determination of carbon dioxide, and, on heating during the second operation, of effectively completing the oxidation of the sample.

METHOD.—The finely-powdered sample (containing 0·05 to 0·1 grm. of carbon) is weighed and introduced into the round-bottomed flask A, fitted with a pipette C, the lower end of which consists of a wide tube drawn out to a point. This flask is connected by a sloping delivery tube with an empty second flask, B, also having a wide entrance tube narrowing at the lower end; a side-tube fitted with an adapter leads to an empty U-tube, and thence to the usual drying tubes of sulphuric acid and absorption tubes of sofnolite and of sulphuric acid. Forty ml. of phosphoric acid, sp.gr. 1·75, are admitted slowly from the pipette, the flask is heated, and the carbon dioxide determined as usual.



Forty ml. of phosphoric acid, in which are dissolved 4 grms. of chromic acid and 0·1 grm. of mercuric oxide, are then introduced into B, and 4 grms. of chromic acid added to A. A current of air is slowly aspirated through the system, and B is gently heated. Just before gas is freely evolved from B a very small flame is placed under A. It is essential that the contents of B should be gently simmering before there are any signs of decomposition in A, and that they should continue to do so until all the decomposition products have been expelled from A. Towards the end of the operation A is heated fairly strongly for 10 to 15 minutes. At the end of an hour the aspirator tap is closed, the burner under A is extinguished, that under B is turned low for a while and then extinguished. When both flasks are moderately cool, aspiration is continued until the absorption tubes cease to gain in weight.

It is important that the temperature of A should be raised only very gradually when frothing is about to commence. There is then very little tendency for the oxidising liquids to be pushed back, owing to the viscosity of the liquids, the width of the tubes, and the mutual "braking" effect of the two columns.

The effect of the mercury is apparently to enhance the activity of the phosphoric-chromic acid mixture while shortening its active life at high temperature. For this reason, the temperature of the second flask is kept as low as is consistent with efficiency, and, further, no mercury is used in the first flask, since it was desirable, especially with the more refractory minerals, to raise the still active oxidising mixture to a high temperature towards the end of the reaction.

The results obtained are shown in the Table, Columns 2 and 3.

Substance	Dry combustion Total carbon Per Cent.	Phosphoric acid treatment Carbon dioxide Per Cent.	Wet combustion Non-carbonate carbon	
			With 2 flasks Per Cent.	With 1 flask Per Cent.
Graphites				
1. Graphite, Ceylon	98·05	nil omitted	97·95	96·34 96·20, 95·35
2. Graphite, Borrowdale ..	—	omitted	87·10	85·49, 85·57
3. Graphite, Canada	75·95	omitted	75·75	—
Bitumens				
4. Kerosene	85·33	omitted	84·16[1,2]	volatile
5. Ozokerite, Galicia	84·33	omitted	84·57[2]	82·41[2]
6. Bitumen (asphalt), S. Australia	83·91	omitted nil	83·68	81·56 60·98, 71·44
7. Native "Pitch" (asphalt), British Guiana	79·41	nil	79·50	74·46
8. Bituminous limestone, Salop	[32·65+8·55[4] =41·20]	[36·90]	1·19 [4·38]	0·82 [3·00]
9. Oil sand, Greece	[11·95]	[4·77]	1·93 [7·08]	1·67 [6·11]
Pyrobitumens				
10. Lignite, Devon	43·83	omitted	43·63	—
11. Cannel, Yorks.	66·07	omitted	66·12	—
12. Coal, semi-anthracite, South Wales[3]	79·68	omitted	79·87	79·09
13. Oil shale, Manvers Main ..	[8·08]	[4·05]	1·10 [4·05]	1·10 [4·00]
14. Potassium acetate (24·45 per cent. C)	—	—	23·40	17·04

REMARKS.—Square brackets indicate percentage of carbon dioxide of sample. All other results are expressed as percentage of carbon.

[1] Eight grms. of chromic acid in each flask.
[2] Heated 90 minutes.
[3] Passed through 250 meshes/inch sieve.
[4] Remaining in ash.

LOSSES FROM THE FIRST FLASK.—An attempt has been made to classify the constituents escaping complete oxidation in the first flask A.

(*a*) *Volatile, probably undecomposed, constituents expelled during heating with phosphoric acid alone.*—The graphites and the pyrobitumens were apparently free from this source of error. In the cases of Nos. 6, 7, 9, and 8 (a bituminous limestone containing an oil, extractable by carbon bisulphide, of composition C, 84·6 per cent.; H, 11·6 per cent.), oily drops, which sometimes solidified, could be seen distilling over into the second flask.

(*b*) *"Cracked" or possibly undecomposed products expelled during heating with phosphoric-chromic acid mixture.*—With bitumens containing difficultly volatile, resistant hydrocarbons, the volatilisation process (*a*) was continued before the acid mixture had time to effect oxidation; *e.g.* No. 5 formed a few oily drops (containing C, 0·7 per cent. of sample) at this stage and No. 7 evolved heavy fumes which later condensed.

(*c*) *Carbon monoxide expelled on heating with phosphoric-chromic acid mixture.*—The oxides of carbon formed from the Ceylon graphite, No. 1, by the two methods were determined by passing the resultant gases through the usual absorption tubes and then over iodine pentoxide.

	Carbon dioxide Carbon Per Cent.	Carbon monoxide Carbon Per Cent.
With 1 flask	96·2	1·1
With 2 flasks	97·95	trace
Dry combustion	98·05	

In order to test the efficiency of the hot phosphoric-chromic acid mixture and mercury catalyst in oxidising carbon monoxide, known concentrations of this gas were passed through flask B and the oxides of carbon estimated. It was found that with comparatively rich mixtures of carbon monoxide (*e.g.* those obtained directly by the decomposition of potassium ferrocyanide, oxalic acid, etc., which is difficult to control), only 75 to 80 per cent. oxidation was attained. When dilute mixtures (not more than a few decigrammes of carbon monoxide per litre of air) were bubbled steadily through the simmering oxidant, all but a trace of the gas was oxidised. These may reasonably be assumed to be the conditions under which the gas is liberated from the sample under analysis.

(*d*) *Partly oxidised products other than carbon monoxide expelled on heating with phosphoric-chromic acid mixture.*—This type of loss was not investigated. It was noticed that when too rapid heating of the flask resulted in undue frothing, a non-oily distillate containing organic carbon was sometimes obtained. Those who have studied the sulpho-chromic oxidation agree that it is probably acetic acid or a similar compound that resists further oxidation in some cases (Simon, *Compt. rend.*, 1924, **178**, 1816; Hall, Miller and Marmu, *J. Chem. Soc.*, **1906**, **89**, **596**). The results obtained for acetic acid, No. 14, indicate that small amounts of this acid, if formed, would be completely oxidised by the proposed method.

SUMMARY.—A wet combustion method, based on the phosphoric-chromic acid process of G. T. Morgan, is described for the determination of carbonate and non-carbonate carbon in rocks and minerals. It has the following advantages:

(i) The operation is simple and completes in one apparatus and on one sample the determination of both forms of carbon.

(ii) All the typical carbon minerals often occurring associated with rocks such as shales, limestones, sands, etc., tested by this method were found to be completely oxidised.

(iii) The method is specially suited to the determination of carbon in rocks containing a considerable amount of carbonate.

The author wishes to thank Sir Robert Robertson for permission to publish this paper.

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Notes

The Editor wishes to point out that the pages of the Journal are open for the inclusion of short notes dealing with analytical practice and kindred matters. Such notes are submitted to the Publication Committee in the usual manner.

THE MICROSCOPICAL EXAMINATION OF HERBS

THE culinary herbs in general use in Great Britain possess many microscopical features by which they may be identified, but when they are mixed together or adulterated with leaves having no aromatic properties, it is essential to have some diagnostic characteristics which afford a means of identifying the various herbs.

During the microscopical examination of a large number of samples it became obvious that among the chief characteristics to which attention had to be directed were the glands and the hairs, and the size of the former and the nature of the latter gave useful proof of the identity of many types of herbs.

The glands vary in size in the different herbs, and the following figures represent many hundreds of measurements made by means of an eye-piece micrometer and a one-quarter inch objective.

MEASUREMENTS OF GLANDS IN LEAVES

	Sage	Thyme	Marjoram	Mint	Basil
Minimum diameter	56μ	62μ	64μ	66μ	66μ
Maximum ,,	72μ	76μ	78μ	76μ	78μ

For the preparation of the leaves for their microscopical examination the method finally adopted was to treat them with warm 2 per cent. alcoholic potassium hydroxide solution, rinse with water, and finally clear by warming with a solution of chloral hydrate. The leaf fragments were then mounted in 30 per cent. glycerin solution, and after such treatment the glands appeared as clear, regular, spherical discs (unless viewed endwise), and, when measuring their diameters, it was noticed that their size bore some relation to that of the stomata on the same specimens.

In general, the measurements of the diameter of the glands showed this to be approximately three times that of the length of the long axis of the stomata, and, when accurate measurements were made, the following results were obtained:

RATIO OF THE MEASUREMENTS OF GLANDS AND STOMATA

	Basil	Mint	Sage	Thyme	Marjoram
Minimum value	2·65	2·80	3·12	3·30	3·64
Maximum ,, ...	2·78	3·00	3·27	3·40	3·74
Average value for all samples examined..	2·72	2·87	3·19	3·33	3·68

Note.—In this table the length of the stomata is taken as unity.

These results were based on the examination of numerous samples of English and foreign-grown herbs, and to confirm the figures for mint (*Mentha viridis*), the plant was grown in London and the leaves from it afforded the following figures:

	Ratio values	Mean
Brown older leaf ..	2·87 2·83 2·88	2·86
Green young leaf ..	2·85 2·95 2·85	2·88

The leaves of both French and Dalmatian sage were examined in this manner, and in every case the ratio was found to be within the above-mentioned limits.

It is essential that as many measurements as possible should be made, both of the diameters of the glands and of the long axis of the stomata, in order to obtain a reasonably accurate average-ratio value.

It should not be inferred that these limits are specific for the respective leaves, but they represent the values obtained with some hundred samples, and recent examinations have confirmed the figures.

I wish to record my thanks to Mr. C. E. Sage, in whose laboratories this investigation was carried out, and to whom I am indebted for permission to publish the results.

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THE COMPOSITION OF THE SATURATED FATTY ACIDS OF JAPANESE CHRYSALIS OIL

Very little has been published on the saturated fatty acids of chrysalis oil. Tsujimoto (*C.I.*, 1908, 1910), in one of his papers on this oil referred to an acid (m.pt. 59° C.; formula, $C_{17}H_{34}O_2$), and suggested that it was probably a mixture of acids of the C_{16} and C_{18} series. Kawase and his co-workers (*J. Soc. Chem. Ind.*, 1921, **40**, 664T), however, isolated an *iso*palmitic acid (m.pt. 57–59°) and palmitic acid from the saturated acids. According to them this *iso*palmitic acid crystallises from alcohol in flat prisms, and both the acid and its magnesium salt are less soluble in alcohol than palmitic acid or magnesium palmitate. Its methyl ester melted at 28° C., and distilled more rapidly than methyl palmitate under reduced pressure.

The sample of chrysalis oil used in our investigation had the following characteristics:—sp.gr. at 15°/4° C., 0·9242; n^{20}_{D}, 1·4750; acid value, 4·0; saponication value, 198·8; iodine value (Wijs), 128·6.

The mixed fatty acids (ca. 700 grms.) prepared from the oil were separated into solid and liquid acids by the lead salt and alcohol method. The solid acids (about 25·7 per cent.) melted at 55 to 56° C., and had neutralisation value 212·8, and iodine value, 14·3. They were methylated in the usual manner, and the esters were separated by fractional distillation under reduced pressure into the following fractions:

Fraction No.	B.pt. (°C.)	Yield Grms.	M.pt. (°C.)	n^{40}_{D}	Iodine value (Wijs)	Sapon. value	Sapon. value (calculated)
1	-180	4	28·5–29	1·4339	4·5	208·1	
2	180–185	11	27·6–28	,,	5·7	208·0	$C_{16}H_{31}O_2CH_3$
3	185–187	30	27·6–28	1·4343	7·3	208·4	=207·57
4	187–189	30	24·8–25·4	1·4347	10·1	205·4	
5	189–191	36	25·1–25·5	,,	12·2	204·3	
6	191–193	20	21·8–22·2	1·4350	16·3	204·0	$C_{17}H_{33}O_2CH_3$
7	193–195	12	21·5–22	,,	19·8	203·9	=197·33
8	195–198	11	21·3–21·6	1·4370	29·0	203·4	
9	198–200	10	22·5–23	1·4392	34·5	195·6	
10	200–202	6	28·3–28·7	1·4408	37·7	195·5	$C_{18}H_{35}O_2CH_3$
11	(Residue)	8	29·5–30	,,	38·1	170·9	=188·07

Sum 178 grms. Loss approx. 8 grms.

A large amount of palmitic acid was separated from fractions 1, 2 and 3, and a small quantity of stearic acid from fractions 8, 9 and 10, but no indication was obtained of the so-called *iso*palmitic acid found by Kawase. The crude fatty acids from fraction 6 were recrystallised thrice from 95 per cent. alcohol and twice from petroleum spirit. The resulting acid (m.pt. 58–58·6° C., neutralisation value 207·6) seemed to be a chemical individual, but it will probably be found to be a mixture of C_{16} and C_{18} acids, as Tsujimoto suggested. Moreover, it is an interesting fact that an acid corresponding with C_{20} or C_{22} was found in the residue.

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FUSED BEADS ON PLATINUM WIRE AS SOLVENTS FOR SMALL PARTICLES OF INSOLUBLE MATERIAL

When a small particle of a substance insoluble in acid has to be dealt with, the usual microchemical methods are not very convenient. Fusion on platinum foil or a small platinum spatula or very small platinum vessel causes creeping of the fusion mixture. I find that the most satisfactory medium is a fused bead on a 0·009 inch platinum wire, the bead being about 1 mm. across. When a fusion has to be undertaken with a nitrate the platinum wire should be twisted into a spiral, 1 mm. in diameter; two turns are sufficient to prevent loss of the bead.

These experiments decided me to try the possibilities of the borax bead as a solvent. Borax has the advantages of dissolving a large number of substances, including many silicates, and of giving a clear bead, so that the completion of solution is obvious. It also enables one to control the saturation of the solution by the size of the bead.

In order to decide what group a substance is in, a bead of microcosmic salt is useful, as it is acid. I prefer a spirit lamp with a small flame for making the bead.

If the bead is placed in dilute hydrochloric acid, the presence of silver is at once shown by a copious amorphous precipitate forming round it. If lead is present, the bead dissolves without separation of lead chloride crystals, but the addition of potassium iodide produces a precipitate. If a borax bead containing lead is placed in potassium iodide solution, crystals of lead iodide are formed on the bead.

If the microcosmic salt bead is placed in a weak solution of hydrochloric acid saturated with hydrogen sulphide gas, a precipitate round the bead of the sulphides in Group II is quickly formed. Dilute acetic acid saturated with hydrogen sulphide gives a white precipitate with a microcosmic salt bead containing zinc. Zinc in a borax bead will give a precipitate with ammonium sulphide.

Ammonium carbonate and ammonia give an opaque bead and a white precipitate with metals of the calcium group. Dilute sulphuric acid gives an amorphous precipitate with barium, and a crystalline precipitate with strontium or calcium.

The various specific reactions sometimes take place on the bead direct and sometimes require previous solution or treatment with hydrochloric or nitric acid. A minute drop from a drawn-out narrow glass tube just sufficient to immerse the bead is used.

An acid solution of potassium ferrocyanide gives a red precipitate with copper, and a blue one with iron. Antimony, tin and bismuth beads yield the appropriate precipitate with calcium chloride and potassium iodide, and the characteristic brown crystals are obtained with a bead containing lead and copper acetate and potassium nitrite. Platinic chloride gives a yellow precipitate with a bead containing potassium.

An important universal reagent in microchemical analysis is potassium mercury thiocyanate. A drop of strong hydrochloric acid is placed on the bead and evaporated to dryness, the undissolved portion of the bead is removed, and the dry salts are dissolved in a drop of water and brought into contact with the thiocyanate reagent on the glass slide.

In order to test for silver with chromate the bead is immersed in a drop of nitric acid and evaporated to dryness; the remainder of the bead is removed, the residue is dissolved in water, and a crystal of potassium chromate is introduced.

In testing for manganese with potassium chromate a sodium carbonate bead is used; it is dissolved in hydrochloric acid, the solution is evaporated to dryness, and the residue is dissolved in water and the solution is tested with a crystal of potassium chromate. This is the only reaction I have found where neither borax nor microcosmic salt is suitable.

A bead containing an aluminium salt forms a red lake if immersed in ammonia containing a little alizarin dissolved in it.

In testing for cobalt with potassium nitrite and for nickel with dimethylglyoxime, the liquid is first evaporated in hydrochloric acid.

Magnesia is best tested for in a microcosmic salt bead: Evaporate with a drop of water, remove the bead, moisten the residue with nitric acid, evaporate again, add ammonia, and scratch the glass with a platinum wire.

The advantages of the bead are: (i) the saturation of the solution is under control; (ii) one drop of solvent, water or acid, is sufficient to dissolve sufficient of the bead to carry out the test, the same bead serving again and again to supply fresh highly concentrated solutions, and where the direct action on the bead of a reagent is possible, the precipitation takes place round the bead, giving the maximum of concentration.

In testing for silica, evaporate with hydrochloric acid, remove the bead, evaporate the residue again with hydrochloric acid, dissolve in water, and add a weak solution of methyl violet; the silica particles are stained and made easily visible.

The metals can easily be electro-deposited from a bead by forming the bead at the end of a straight platinum wire, immersing it, together with another wire, in a conducting solution, and connecting the two wires with a source of electric current. The bead is rapidly dissolved and the metals deposited on the wire, the maximum concentration being thus obtained. The microcosmic salt bead should be used only for special reactions, as it introduces phosphates. The presence of borates and boric acid from the borax bead does not seem to interfere with the reactions given above. Where a neutral bead is required, the borax and microcosmic salt can be mixed in the proper proportions.

Obviously, the method is equally applicable to the many specific tests now available with organic reagents.

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THE DETECTION OF SMALL QUANTITIES OF GERMANIUM IN THE PRESENCE OF ARSENIC

IN a previous communication (ANALYST, 1934, 462) a new electrolytic method for the determination of small quantities of germanium in the presence of arsenic was described.

The present investigation was carried out to determine whether the existing chemical methods of reduction can be improved, and, in particular, be adapted for the determination of germanium when arsenic is present. Müller and Smith (*J. Amer. Chem. Soc.*, **1922**, **44**, 1909) have detected 0·06 mgrm. of germanium in the Marsh type of apparatus using sodium amalgam as a source of nascent hydrogen; with aluminium and potash they found that 5 mgrms. of germanium dioxide were needed to give a mirror. The detection in the presence of arsenic was not considered.

METHOD.—The apparatus consisted of a round-bottomed flask to which was attached an air condenser, which in turn was connected with a decomposition tube. Into the flask was led a stream of hydrogen gas obtained from a cylinder, the gas passing through a safety trap and a bubbler. The flask was also fitted with a dropping funnel for the introduction of alkali and germanium solution after the apparatus had been filled with hydrogen.

1. REDUCTION WITH SODIUM AMALGAM.—Twenty-five grms. of sodium amalgam containing about 3 per cent. of sodium, were placed in the flask, and, when the apparatus had been filled with hydrogen, the solution to be reduced and 10 ml. of 10 per cent. sodium hydroxide solution were added through the dropping funnel. Then the decomposition tube was heated to redness, the flask gently warmed until a brisk evolution of gas resulted, and the rate of hydrogen passing was adjusted to about three bubbles a second. Blank tests showed the materials in use to be free from any mirror-producing substances.

Detection of Small Quantities of Germanium.—In this way a definite metallic deposit was obtained in the combustion tube with 0·05 mgrm. of germanium dioxide in 25 minutes. A smaller quantity did not give satisfactory results.

Standard mirrors were prepared from quantities of germanium dioxide ranging from 0·05 mgrm. to 0·1 mgrm., and by matching it was found possible to differentiate between quantities of dioxide varying by 0·01 mgrm.

Detection in the Presence of Arsenic.—As with the electrolytic method, arsenic present as an arsenate was found not to be reduced, and the expected germanium stain was obtained. (For oxidation of arsenite to arsenate, see ANALYST, 1934, 462.) A quantity of 120 mgrms. of potassium arsenate was found not to interfere with the deposition of germanium.

2. REDUCTION WITH ALUMINIUM AND POTASSIUM HYDROXIDE.—In this reduction the action is so vigorous that the procedure was varied slightly. Three grms. of aluminium turnings were placed in the flask, the germanium solution was added, and potassium hydroxide (23 grms. in 100 ml. of water) was introduced, drop by drop, through the funnel. No mirror was obtained with amounts of germanium dioxide less than 0·16 mgrm.

3. SOME OTHER REDUCING SOLUTIONS.—Devarda's alloy was ineffective with as much as 10 mgrms. of germanium dioxide. Hydroxylamine hydrochloride was also tried, but did not reduce 10 mgrms. of germanium dioxide, whilst hydrazine sulphate did not reduce 2·25 mgrms. of the dioxide.

CONCLUSION.—The amounts of germanium dioxide which may be estimated by the methods described are as follows:

(i) Electrolytic method: 0·027 mgrm. in steps of 0·01 mgrm. of GeO_2 up to 0·1 mgrm. of GeO_2.

(ii) Sodium amalgam: 0·05 mgrm. in steps of 0·01 mgrm. of GeO_2 up to 0·1 mgrm. of GeO_2.

(iii) Aluminium and potassium hydroxide method: least amount of GeO_2 detected = 0·16 mgrm.

Only methods 1 and 2 are recommended for purposes of analysis.

When using either of these methods, series of standard mirrors must be prepared by the method and with the apparatus to be employed. In both cases differences of 0·01 mgrm. of GeO_2 can be recognised. The maximum amount of germanium dioxide which I have used in any one experiment by the electrolytic or sodium amalgam method is 0·1 mgrm., and it is recommended that when larger amounts than 0·1 mgrm. are present in the test, an aliquot part be taken to bring the amount below this figure.

In no case is all the germanium which is placed in the solution recovered in the mirror, but this circumstance does not detract from the usefulness of the method, when care is taken to carry out experiments on the substance of unknown composition in the identical way employed for making the standards. Both the methods may be employed in the presence of arsenic in the quinquevalent condition.

I should like again to express my indebtedness to Dr. H. J. S. Sand for the continued interest which he has taken in the work.

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THE USE OF ULTRA-VIOLET LIGHT FOR THE DETECTION OF TRACES OF SULPHIDES

THE method described by Grant and Booth (ANALYST, 1932, **57**, 514) has been used successfully for the detection of sulphides. The only modification which is applicable is the use of 0·5 ml. of a saturated solution of quinine in water instead of the solid alkaloid; a minimum quantity of quinine should be used in order to ensure the formation of the acid sulphate, which has a more intense fluorescence than the normal salt. The maximum sensitiveness of the test is 0·1 mgrm. of sulphide sulphur, added in the form of a dilute solution of sodium sulphide (1 ml. = 1 mgrm. S.). This was standardised by means of the colour produced, in the presence of ammonia, with a standard solution containing lead. In this connection an attempt was made to find the limiting concentration necessary for the production of the fluorescence of quinine sulphate. It was found that if 0·01 N sulphuric acid was added drop by drop to about 15 ml. of a solution of the quinine in a test tube, and this was illuminated horizontally by transmitted filtered ultra-violet light and viewed vertically, a faint blue fluorescence was visible in solutions containing $1 : 0{\cdot}5 \times 10^8$ of quinine. If one excepts X-ray methods, this would appear to be one of the most sensitive tests known.

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ULTRA-VIOLET LIGHT AS A MEANS OF DETECTING ARTIFICIAL WATERMARKS

ARTIFICIAL watermarks usually fall into one of two classes, *viz.*:

(i) Those produced by stamping the finished paper with an oily medium which creates the impression of transparency. Such watermarks are usually removed by extraction with ether, and, owing to the presence of oily matter, fluoresce vividly in filtered ultra-violet light, whilst genuine watermarks remain invisible, or at the most appear in dark outline. Frequently the fluorescence is enhanced after the process of extraction with ether, whereas with genuine watermarks there is no alteration.

Artificial watermarks of this type are comparatively easy to recognise, and an application of the method to the detection of a banknote forgery has already been described (ANALYST, 1933, **58**, 603).

(ii) In the second type of imitation watermark an impression is produced on the paper before it is completely dried, by means of a circular rubber band carrying the design in relief. It differs from the genuine watermark only in that the latter is applied to the wet pulp on the machine wire before it really becomes paper, and consequently it is more difficult to identify than the first type mentioned above.

The method now suggested for this purpose depends on the fact that, although both the genuine watermark and the artificial watermark of the second type depend on producing a thin place in the paper, in the former case the wet pulp is squeezed aside from the places where the impression falls, whilst in the latter the almost dry paper is compressed into a denser form. Water will, therefore, penetrate more rapidly through the genuine watermark than through the imitation design, although the thickness may be identical.

The procedure is as follows:—Ordinary icing sugar is dried in the oven, and a mixture of 100 grms. with 0·5 grm. of Rhodamine-6G (concentrated) is ground well in a mortar and transferred to a small bottle provided with a metal screw-cap, the top of which is inset with a piece of 70-mesh bronze gauze so as to form a "pepper-box"; when not in use, the bottle and its contents should be kept in a desiccator containing calcium chloride.

For the actual test the mixture is sprinkled uniformly in a thin layer over the watermark and adjacent portions of the paper, so that the surface just remains visible, and the paper is then placed in a dish of water under a source of filtered ultra-violet light in a dark room. Complete penetration of the water through the paper is indicated by a bright golden fluorescence due to the solution of the dye. With the genuine watermark only, this is found to occur most rapidly through the watermark, the design of which stands out vividly against a dark ground for a few seconds before the remainder of the sheet is penetrated. With imitation watermarks, however, the rate of penetration is uniform throughout the sheet.

This method has also been applied to the determination of the degree of sizing of paper in terms of its resistance to penetration by water, and an end-point is obtained which is considerably sharper and more consistent than those provided by existing methods. Full details will be published shortly.

I am indebted to the Directors of Messrs. John Dickinson & Co., Ltd., for permission to publish these results.

JULIUS GRANT

THE LABORATORIES
CROXLEY MILLS, HERTS

Official Appointments

THE Minister of Health has approved the following appointments:

FREDERICK DIXON as a Public Analyst for the County Borough of Stoke-on-Trent, in addition to Ernest Victor Jones (October 5th).

THOMAS REGINALD HODGSON as a Public Analyst for the County Borough of Stockport, in place of William Marshall (deceased) (October 15th).

Notes from the Reports of Public Analysts

The Editor would be glad to receive the Annual or other Reports of Public Analysts containing matter of special interest to the Society. Notes made from such Reports would be submitted to the Publication Committee.

CITY OF BIRMINGHAM

Report of the City Analyst for the Second Quarter, 1934

Of the 1426 samples of food and drugs submitted during the quarter, 91 were bought informally. The total number of adulterated or incorrect samples was 96.

Grape Fruit Butter.—This article, the name of which suggests that a fair amount of butter is present, was found to contain only 2·5 per cent. In appearance and taste it resembled lemon cheese, but in so far, at least, as the fat-content was concerned, it was inferior to the average sample of this commodity, which usually contains about 10 to 15 per cent. of butter. The use of the word "butter" as part of the description of this article would appear to be misleading and unjustifiable.

Table Vinegar.—A sample bought as table vinegar was supplied in a bottle labelled "Table Vinegar. Absolutely Pure Wood Vinegar." Table vinegar should consist of malt vinegar, and such a label as the above is a contradiction in terms. The packers were cautioned.

"Double-Strength" Tea.—The label on a sample of tea stated: "One teaspoonful will more than equal two teaspoonfuls of ordinary tea." The amount of extract given by boiling the tea with water was 40 per cent.—a perfectly normal figure, showing that, to make the usual infusion, about the same quantity of the sample would be required as of any other tea. The packers agreed to delete the words in question from the labels. The label on another sample of tea stated that a half-pound would go as far as one pound of ordinary tea and, in addition, the article was described as "double strength." The total boiling-water extract in this case was 42 per cent., which is, again, a normal figure. Representations have been made to the firm concerned.

H. H. Bagnall

CITY AND COUNTY OF BRISTOL

Annual Report of the Public Analyst for the year 1933

The number of samples submitted for analysis was 1375, and of these 69 were adulterated.

British Wines and Unfermented Cordials.—Two samples of British wine and six of unfermented cordials were examined, and the following results were obtained:

Description	British Wine		Unfermented Cordial		
No.	514	517	Lowest	Highest	Average
Sp.gr. at 15·5 °C.	1021·9	1076·0	1055·3	1273·1	1116·7
Alcohol by wt., per cent.	12·23	9·11	0·16	0·70	0·38
Alcohol by vol., per cent.	15·12	11·30	0·19	0·88	0·47
Total solids, per cent. ..	8·90	22·54	14·28	60·42	27·80
Ash, per cent.	0·313	0·150	0·005	0·10	0·053

Sulphur dioxide was present in one of the British wines, the amount being 0·036 per cent., but it was not found in the unfermented cordials. Two of the latter, however, contained 0·07 per cent. of benzoic acid and were condemned, while two others contained 0·05 and 0·022 per cent. respectively. Saccharin was detected in three of the unfermented cordials.

LEMONADE TABLETS.—A sample submitted by the Port authority consisted of 96·5 per cent. of citric acid, with colouring matter, but no sugar. It was free from sulphur dioxide and contaminating metals.

E. RUSSELL

Palestine

ANNUAL REPORT OF THE GOVERNMENT ANALYST FOR THE YEAR 1933

IN his Annual Report, the Government Analyst (Mr. G. W. Baker) states that 9965 samples were examined, and that, in addition to routine work, investigations for the Department of Agriculture and Forests, and for the Research Department, Woolwich, had been continued, and that an investigation on counterfeit coinage had been completed.

EDIBLE FATS AND OILS.—Of the 1332 samples, 1060 were of imported goods. Seventeen of 74 samples of local semni were adulterated, mainly with fat of the coconut type. Twenty-one of 81 olive oils were adulterated, the adulterant being sunflower seed oil (15), arachis oil (5), and sesame oil (1).

POISONING CASES.—Sixty-nine specimens were examined in connection with 18 cases of supposed human poisoning, and in 11 of these poison was found, *viz.* veronal (2), lysol (2), thallium (2), arsenic (3), cyanide (1), alcohol (1).

Thallium Poisoning.—The cases of thallium poisoning occurred near Beersheba, where a mother and two children, aged 4 and 7, inadvertently ate some poisoned wheat imported for the destruction of field mice (*cf.* ANALYST, 1933, **58**, 547). Twelve hours later vomiting started with slight purging and pronounced abdominal pains, and the elder child, who, it was said, had eaten more of the wheat than his sister, continued to show these symptoms, and died on the fifth day, without medical attention. The younger child was comatose when seen on the eighth day, and died on the ninth day. The mother's symptoms were less severe. and, so far as is known, she eventually recovered. The father did not report the matter until three days after the death of the elder child. Thallium was detected in the portions of viscera submitted, and also in a sample of the "Zelio" grains of which they had eaten.

EXHIBITS IN CASES OF SHOOTING.—All exhibits are now first examined at the central offices of the C.I.D., and are only subsequently examined by the Government Analyst when chemical work is necessary or a confirmatory opinion is required.

Such exhibits totalled 89, as compared with 250 in 1932. They included firearms (4), bullets (24), cartridge cases (25), other related exhibits (36). In one case examination of a fragment of paper and fibre from a wound yielded presumptive evidence that a single ball 16-bore cartridge was concerned. In another instance there was evidence that the composition of the lead in confiscated bullets differed from that in bullets from the scene of the crime. In another case it was shown that four 12-bore cartridge cases were all fired from one shot gun. Eight exhibits were connected with bomb-throwing. In one case traces of potassium chlorate were detected in fragments of the exploded bomb.

Drug Traffic.—In one case of alleged traffic in hashish, two samples of wrapping paper have been submitted for examination. One of these (A) was found in a suspect's house in Palestine and one (B) in a neighbouring country to which it was suspected that hashish had been smuggled. A physical and chemical examination showed that two kinds of paper were present in sample "B". The fluorescence test was of value in this case. Petroleum spirit extracts, from portions which showed green stains in ultra-violet light, gave positive reactions with Beam's test for hashish.

Counterfeit Currency.—At the request of the Palestine Currency Board an examination of 763 coins was undertaken with the object of discovering evidence as to origin and other facts which might be of use to the Police. The coins in question had been impounded as counterfeits by the Treasury, and had been tendered, mostly at railway booking offices, over a period of 26 months. A representative selection of 69 coins was sent to the Comptroller at the Royal Mint, whose report included the information that 14 of the coins were struck from 4 pairs of dies and that the remainder were cast coins, mostly from plastic moulds, and a few from metal moulds. The findings in these Laboratories, combined with those at the Mint, classified 262 coins (all 50 mils) as struck counterfeits, five as genuine coins, and the remainder as cast counterfeits, some of which were crude attempts in soft metal.

By low-power microscopical examination, after cleaning with dilute ammonia, and by photography giving a magnification of about 3 diameters in oblique illumination, it was possible to identify by characteristic faults in the coins nine different dies, and it was, moreover, possible to show that at least 5 of these dies, accounting for 67 per cent. of the struck coins, were in the hands of one group of counterfeiters. The weights and diameters of these struck coins were in most cases approximately correct, but the silver-content was considerably higher than that in the genuine currency. Tests carried out showed that, when tendered, they would generally deceive any but experienced cashiers on the look-out for such counterfeits.

Siam

SIXTH REPORT OF THE GOVERNMENT LABORATORY

(From April 1st, 1930, to March 31st, 1932)

The Report of the retiring Director (Mr. A. Marcan, F.I.C.) to the Ministry of Commerce and Communications summarises the official work of the two years since the last report (Analyst, 1932, 57, 312). The number of samples examined (9193) shows a large increase, owing to additional routine work in connection with opium dross and mint assays for silver.

Drugs for the Treatment of Leprosy.—Clinical tests showed that the ethyl ester derived from *Taraktogenos ilicifolia* (*Hydnocarpus il.*; *cf.* Analyst, 1932, 57, 313) caused much pain on injection, and led to a rise in temperature lasting for 1 or 2 days, whereas the esters from *H. anthelmintica* were painless in use and produced results similar to those given by the esters of *H. Wightiana*, which is the species mainly used in India. Further efforts are being made to produce *ilicifolia* oil suitable for injection, since the esters are not satisfactory.

Physiological Action of Kratom.—Mitragynine acetate prepared from kratom leaves (*Mitragyne speciosa*) was sent to Professor Barger and to the late Dr. Dixon at Cambridge for pharmacological tests. It was found to diminish the excitability of plain muscle, to anaesthetise the cornea, and to be toxic to animals in fairly low doses. In its effect upon the nervous system it resembles cocaine, but there is nothing to suggest that it is effective as an antiseptic against bacteria or pathogenic protozoa. The results afforded no explanation of its action as a drug of addiction.

In the psychological research six human subjects submitted to various laboratory tests after taking doses of 50 to 100 mgrms. of mitragynine acetate and after doses of 0·65 grm. to 1·3 grm. of the powdered leaves. There were indications that both forms of the drug produced the following effects:—Decrease in the time of reaction to stimulus; increased tolerance to heat; increased steadiness and capacity for work; flushing of the skin, apparently due to dilatation of superficial blood vessels. These effects agree with those reported in a survey of the use of the drug in Siam (*cf.* ANALYST, 1929, **54**, 475).

SEEDS OF STRYCHNOS SPP.—Two varieties of *Strychnos* seeds containing 1·99 and 1·89 per cent. of strychnine, respectively, have been examined in London and found to be suitable for the manufacture of the alkaloid. Although the exact species to which these two varieties of seeds belong is not yet certain, it is different from *S. nux vomica.* A sample of seeds locally termed "Phya mu lek," was found to be *Strychnos roborans*, and contained no strychnine. Another species recently examined was *S. nux blanda*, and also contained no strychnine. Samples from Burma have been examined elsewhere with similar results, and the seeds are sometimes known as "False nux vomica."

SEEDS OF "SAKAE COMBRETUM QUADRANGULARE."—The seeds of this plant have a local reputation as an anthelmintic, and a sample was sent to England for physiological test several years ago. Dr. T. A. Henry came to the conclusion that the active principle was in the tannin-free water-soluble extract, but this was reported to be without effect on hookworm in dogs by Dr. S. Pessôa of the Instituto de Hygiene, San Paulo, Brazil.

Prof. B. A. McSwiney, of the School of Medicine, Leeds, working with the same extract, found that it was effective only in high concentration (0·5 grm. of seeds per ml.) when tested on round worms *in vitro.* He considered the active principle to be similar to that of *Combretum pilosum*, which also has a reputation as an anthelmintic in India.

In order to provide further material for these tests a quantity of Sakae seeds was extracted with alcohol in the Technical Laboratory, and 0·92 kilo. of dry extract has been sent to Prof. McSwiney.

BARK OF "PICRASMA JAVANICA."—*Picrasma javanica* is a small tree found in the evergreen forest in Northern Siam. The bark has a considerable local reputation as a febrifuge and possesses a bitter taste resembling that of quinine. A small sample had been examined in India and had been reported to contain 0·1 per cent. of an alkaloid resembling quinine.

In Bangkok the bark was extracted with a number of solvents, and it was proved that the active principle was not quinine, although it gave certain reactions for alkaloids and exhibited fluorescence in aqueous solution.

CHINESE EDIBLE BIRD'S NESTS.—A sample of edible bird's nests, a prized luxury food of the Chinese, was submitted by the Rural Economic Survey from Chumporn. The analysis was as follows:—Moisture, 16·3; protein ($N \times 6{\cdot}25$), 49·8; fat, 0·06; ash, 7·5; water-soluble ash, 5·4 per cent. The ash contained a considerable amount of lime.

EDIBLE SPIDERS.—Some spiders used as food by Lao people were submitted privately by a scientist travelling in the country. The species was described as *Lamphopelma siolaceopides.* The analysis which follows shows that they form a rich nitrogenous food:—Moisture and volatile matter, 12·1; fat, 9·8; nitrogen, 10·1; ash, 5·3 per cent.

Trinidad and Tobago

ANNUAL REPORT OF THE GOVERNMENT ANALYST FOR THE YEAR 1933

In his Annual Report Mr. H. S. Shrewsbury gives an outline of the work undertaken for various Government Departments, including Constabulary, Customs and Excise, the Surgeon-General, Public Work, and the British Admiralty.

FOOD AND DRUGS ORDINANCE.—Samples are submitted by officials of the Police or the Preventive Officers of the Customs and Excise Department. Of the 1865 samples submitted, 77 were adulterated; these were mainly milk and watered rum.

Saccharin in Aerated Waters.—Two aerated waters contained saccharin and four contained an excessive quantity of lead. It is pleasing to be able to note that there has been almost a cessation of the practice of using saccharin in aerated waters of local manufacture, this being due in a large measure to its use being prohibited under the Ordinance, and the consequent co-operation between the Constabulary and this Department in frequently purchasing and analysing aerated waters and prosecuting vendors whose drinks were found to contain saccharin. Out of 602 sweetened aerated waters taken by officials from all the police stations in the Colony, only two were found to contain saccharin, the vendors in each case being prosecuted, convicted and fined. The percentage of sweet drinks thus found to contain saccharin was only 0·2, as compared with 7·5 for 1932.

Department of Scientific and Industrial Research

REPORT OF THE BUILDING RESEARCH BOARD FOR THE YEAR 1933*

THE Report of the Board (pp. 1–4), which is signed by the Chairman (Sir Raymond Unwin), deals in outline with the progress of the work by the various Committees, and with the co-operative research initiated in conjunction with other organisations. This is followed by the report of the Director of Building Research (Dr. R. E. Stradling) (pp. 5–104), Intelligence and Minor Investigations (pp. 104–124), an account of the activity of the library (pp. 125–126), appendices giving the staff and a list of reports, etc., published during 1933, and an index (pp. 135–139). There are 43 figures and 20 tables.

Among the items of special interest are the following:

WEATHERING OF BUILDING STONES.—In the main, attention has been confined to the limestones, and the fundamental idea underlying their investigation in the laboratory is that their durability depends in the first place on physical structure rather than on chemical composition.

Portland Stone.—By means of tests on samples of known quality it has been found possible to classify Portland stone in quality groups by measuring total micro-porosity and saturation coefficient. The method of determining the former property was described in the Report for 1931. "Saturation coefficient" is a term used by Hirschwald (*Handbuch der bautechnischen Gesteinprüfung*, Berlin, Gebrüder Borntrăger), and signifies the ratio between the amount of water absorbed by simple soaking for a standard time and the accessible pore space. As a general rule, a material having a coefficient of less than 0·80 is unlikely to be damaged by frost. Recent research, however, has shown that the saturation coefficient is intimately linked with the structural characteristics of the stone, and through them with its general weathering behaviour, apart from the question of frost. A chart is given showing the mean relationship between micro-porosity and saturation coefficient, as calculated from the results given by 165 samples of the normal type of Portland stone, which is characterised by the presence of large inter-connected pore-spaces between the oolitic grains and the lack of a continuous crystalline matrix, such as is found in many oolitic limestones. By measuring micro-porosity or saturation coefficient, or preferably both, a quarry sample can thus be compared with samples of known quality, and it may be inferred that its weathering quality will resemble that of the standard sample with which it most nearly corresponds in these physical characteristics. In applying these tests the practical way is to sample the quarries systematically, and thus to establish the position of the deposits of good and inferior quality.

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* H. M. Stationery Office, Adastral House, Kingsway, W.C.2., pp. 139, Price 2/6 net.

Clipsham Stone.—Clipsham stone is quite different in structure from Portland stone; it is a partly shelly and partly oolitic limestone, in which the relative amounts of shells and oolitic grains vary greatly. So far it has not proved possible to relate micro-porosity, as arbitrarily defined for Portland stone, with the saturation coefficient. But it has been found that quality, as judged by the crystallisation test, tends to decrease with increase in the saturation coefficient.

With Clipsham stone, it is necessary to distinguish two types, and, although there is no sharp dividing line between the one and the other, the two types are more or less readily identifiable by inspection. One type is predominantly shelly, the other is much more oolitic in character. Laboratory tests have led to the conclusion that the more shelly type of stone is of superior weathering quality.

These conclusions have been borne out by the observations of builders and masons. In two buildings marked decay associated with efflorescent salts has been observed. The deleterious salts have affected the oolitic stone much more seriously than the shelly stone, and in one of the buildings where this difference is particularly pronounced the decaying stone has been in position only two years. It is understood that the old masonry was cleaned with an alkaline solution when the repairs were executed. The resulting decay furnishes an illustration of the dangers associated with the use of chemicals for cleaning masonry, and to which attention has been repeatedly directed in previous Reports.

The Crushing Strength of Building Stones.—It cannot be too strongly emphasised that the properties of building stones commonly quoted in trade advertisements, and on which architects are presumably invited to form an opinion of quality, often afford no criterion of durability at all; the figures may, in fact, be quite misleading. Crushing strength is a notable example. For instance, it is shown that certain stone of such poor quality that it had suffered excessive decay through exposure for 20 years in London, had nearly twice the crushing strength of stone that had weathered perfectly for 250 years in St. Paul's Cathedral.

Atmospheric Pollution.—Tests on the lead peroxide method of estimating sulphur pollution (*The Investigation of Atmospheric Pollution*, 18th Report, 1933, p. 14, *cf.* ANALYST, 1933, **58**, 284) have been continued. The method is now in regular use in 34 stations, and is also being employed in connection with research on the corrosion of non-ferrous metals, the durability of leather in libraries, and the recording of pollution emanating from a localised source.

Physical Factors influencing Weathering.—In the tests on pressure deficiency and the water-content of stones it has been found that a centrifugal method gives results closely comparable with those obtained by the hydrostatic method (see Report for 1931). By determining the relative amounts of water held at equilibrium in two different stones in contact it is possible to deduce the direction of transfer between one stone and another and to demonstrate differences between different types of stone.

Frost Action.—Laboratory specimens of building materials were subjected to an accelerated test in which the samples were soaked in water and then subjected to a maximum of 50 cycles of alternate freezing in air to about −20° C. and thawing in tap water. Each freezing and each thawing lasted for 24 hours. On the roof duplicate specimens were exposed in two different ways; in one the specimens rested half-immersed in water in a tray, and in the other they simply stood on the roof. During the winter of 1932–33 they were exposed to 77 frosts of not less than 2° F.

Several types of bricks were not affected by any of the tests, while others showed marked and rapid disintegration both on the roof and in the laboratory. There were, however, several types which, although they remained sound during the one winter's exposure, failed badly when frozen artificially. It is too early as yet to say whether the latter results are actually anomalous, since some of the exposed bricks may fail in the near future. There are good grounds, nevertheless, for supposing that in certain cases the laboratory test produced effects which are unlikely to result from natural frost.

Nine different varieties of Bath stone were tested by natural exposure tests under varying weather conditions on the roof. Day-to-day measurement of the moisture-content of other similarly-exposed specimens of the same size has shown that, under these conditions, even materials which are known to be very susceptible to frost are seldom sufficiently saturated with water to suffer much damage.

The specimens standing in water, on the other hand, were damaged to varying extents, and it was found that the specimens which suffered the most were those with saturation coefficients greater than 0·80. Those with saturation coefficients below 0·80 did not suffer any significant damage, even under these somewhat severe conditions.

Notwithstanding these results, it is still believed that frost plays a subsidiary part, as compared with the effect of smoke gases, in the weathering of calcareous stones in this country.

Effect of Soluble Salts.—Stones impregnated with sodium compounds—hydroxide, carbonate, sulphate, and peroxide—have continued to show serious decay. Appreciable, but less pronounced, decay has occurred in specimens treated with ammonium salts. Potassium salts, sea-water salts and sodium carbonate have caused little, if any, decay.

The effective life of certain of the materials commonly employed as stone preservatives is limited to about 12 to 18 months. Instances are cited in which treatment has even hastened decay.

Chlorides in Portland Stone.—Tests, supplemented by observation of the behaviour of blocks in a London building, suggest that Portland stone of poor quality is much more affected by the presence of chlorides than stone of good quality. Recent observations suggest that contaminated stone is seldom, if ever, to be found in the quarries, except in those where the stone may be washed by the sea.

Relation of Micro-Organisms to the Decay of Stone.—Experiments have proved that rain water and the sulphur gases of the laboratory can provide sufficient nutriment to support the life of micro-organisms on the surface of stone. It has recently been found that a water extract of sound stone, when added to a crude culture of stone organisms in a solution of sodium thiosulphate, enhances the rate of oxidation of thiosulphate, as compared with the water control. It can be assumed, therefore, that the stone contains a significant supply of food material for such organisms as these—(*cf.* Paine *et al.*, *Phil. Trans. Roy. Soc.*, 1933, **222** [B], 97).

MATERIALS.—*Asphalts and Bitumens.*—Experiments (described in detail) indicate that it is probable that blisters on asphalt roofs are caused by the thermal expansion of water vapour or air entrapped by moisture in the pores of the concrete beneath the mastic. Their formation appears to be preventable by reducing the moisture-content of the concrete, by eliminating condensation and absorption of water, by using concrete with coarse pores, or by inserting a layer of felt, paper or the like to prevent the asphalt from adhering to the concrete. The first suggestion is the simplest for application to existing roofs, and the third for new roofs or those being entirely re-laid.

Cement.—Direct deductions from data embodied in a diagram of the system—Lime-Alumina-Silica-Ferric Oxide—confirm the view that ferric oxide in Portland cement exists in the form of the compound $4CaO.Al_2O_3.Fe_2O_3$, and show that in cements made from CaO, Al_2O_3, SiO_2 and Fe_2O_3 only, melting begins at 1338° C.

Considerable attention has been given to the attack of concrete by soil waters and by clays containing sulphates. Tests have indicated that neither removal of the free calcium hydroxide, nor the change of the hydrated silicates and aluminates by autoclaving is alone sufficient to effect more than a partial increase in the resistance to sulphate action. When both occur together the improvement is great.

Keene's Cement.—According to his last patent (1838) Keene made his plaster by burning gypsum, adding potash alum as an accelerator, and then reburning and grinding. Other methods are now used, the products differing in properties according to the method of manufacture, but it would appear that no product should be termed "Keene's" unless it possesses the properties of the original product. Unfortunately it has proved impossible to obtain any definite agreement as to what were the essential properties of the original Keene's cement. It is hoped that the proposed specification, by providing a means of differentiating between different types of plaster, will tend to remove some of these difficulties.

Roofing Slates.—The effects of cycles of wetting and drying on a representative series of slates have been studied by soaking the specimens in water for 6 hours at laboratory temperatures and drying for 18 hours in an oven at 110° C. In certain cases the process has been repeated as many as 200 times. The results of the tests are set forth in a table, which also gives the carbon dioxide and sulphur-contents and the results of acid tests. In general, the effects resemble those observed when the specimens are immersed in acid.

Slates that bear the best reputation for durability and contain only negligible quantities of pyrites have been found to withstand more than 100 cycles without being affected, though in some cases lamination may ultimately occur. On the other hand, slates that are attacked within about 20 cycles thereafter decay very rapidly. Specimens of such slates contained from 3 to 3·46 per cent. of ferrous sulphide.

Florescence in Bricks.—Research on florescence has been concerned mainly with the question of the permissible limits for the salt content of bricks. The problem is complex because the capacities of the various salts for causing trouble are very different. A brick containing 0·1 per cent. of water-soluble magnesium in the form of sulphate (about 1·0 per cent. of hydrated magnesium sulphate) would almost certainly cause the failure of plaster applied to it, but an equal amount of calcium sulphate might be quite innocuous. A further complication is introduced by the texture of the brick. If a brick is soft and highly porous through underfiring, water will easily gain access to any soluble material it may contain, and recrystallisation of these salts near the surface may cause flaking.

The crystallisation test, described in the last Report, is used as a means of estimating the intrinsic resistance of the material to disruption by the action of soluble salts.

Other points discussed in connection with materials include the durability of bricks underground, the thermal expansion of plate glass, paints, and water proofers. "The Structure and Strength of Materials" forms a section of thirty pages, and "The Efficiency of Buildings from the Standpoint of the User" is discussed under various headings, reference being made to the investigation of the question of infra-red rays and comfort, of which an account has been published (Dufton, *J. Hygiene*, **1933**, **33**, **476**).

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs Analysis

Transmission of Light by Egg Albumin. H. J. Almquist, J. W. Givens, and A. Close. (*Ind. Eng. Chem.*, 1934, **26**, 847–848.)—The transmission of light varies in different layers of egg albumin, being lowest in the firm or gelatinous layer; it is correlated with the percentage of mucin in the albumin, and varies with the temperature and p_H value, which affect the physical condition of the mucin. The changes thus produced cause differences in the candling appearance of eggs, which are not necessarily due to changes in interior quality.

W. P. S.

Formaldehyde in Canned Marine Products. G. Lunde and E. Mathiesen. (*Ind. Eng. Chem.*, 1934, **26**, 974–976.)—Canned marine products frequently give a positive reaction when tested for formaldehyde by the official tests of the Association of Official Agricultural Chemists. The official tests, in which phenylhydrazine hydrochloride is used as a reagent, cannot be applied directly to liquid foods or aqueous extracts of foods which may contain trimethylamine. The trimethylamine naturally present in fish foods causes a positive reaction in these tests. Of other tests used, only the Hehner test could be satisfactorily applied directly to an aqueous extract of fish, although all the tests could be used on the distillate from an acid distillation. Formaldehyde has been detected in the distillate from fresh and canned herring, crab and other marine products. The amount found in the canned food is somewhat higher than in the fresh fish. The formation of formaldehyde in canned fish appears to be independent of the nature of the container and does not increase during storage. The formaldehyde is not formed during the distillation process, as it can be detected in an aqueous extract of the fish by means of the Hehner test. S. G. S.

Iodine-reducing Value of Orange Juice. M. A. Joslyn and G. L. Marsh. (*Ind. Eng. Chem.*, 1934, **26**, 857–860.)—Loss in the iodine-reducing value of orange juice is due to oxidation and is not caused by the action of preservatives of the benzoate type or by heat treatment in the absence of air. W. P. S.

Determination of Citric Acid as Pentabromoacetone and its Application to Wine. O. Reichard. (*Z. Unt. Lebensm.*, **1934**, **68**, 138–172.)—The conditions for the quantitative conversion of citric acid in aqueous solution into pentabromoacetone have been established. The treatment with potassium bromide, sulphuric acid and potassium permanganate must be carried out at a temperature not higher than 5° C., and bromine must be present in such quantity that the ratio bromine: citric acid is not less than 2, and the ratio potassium bromide : citric acid not below 3. The amount of potassium permanganate present must produce a persistent violet colour or a separation of manganese dioxide. After being washed with water, the collected pentabromoacetone is dried for 2 hours in a desiccator over sulphuric acid. It may be identified by the melting-point (71° to 72° C. for the crude, and 73° C. for the purified product), the crystalline form, the colour reactions with resorcinol and phloroglucinol, and, after decomposition by alkali, by the isonitrile reaction.

In the amounts occurring in wines, glycerol and such organic acids as malic, lactic, tartaric and acetic acids do not interfere with the determination, provided that the above conditions are fulfilled; preliminary separation of the citric acid is usually unnecessary. The presence of more than 5 grms. of sugar per litre renders direct bromination of the citric acid impracticable. In this case either the sugar is first fermented away or the citric acid is precipitated as barium salt, which is washed with 50 per cent. (by vol.) alcohol and subsequently brominated. With both red and white dry berry and grape wines, with and without added citric acid, the method gives accurate results. With a dry wine containing only little citric acid, precipitation of the barium salt, followed by bromination, is advisable. Details are given of the procedure to be followed in the various cases.

T. H. P.

Detection of Sorbitol in Fruit Products. G. Reif. (*Z. Unt. Lebensm.*, 1934, **68**, 179–186.)—The removal of fruit constituents which interfere with the reaction of sorbitol with benzaldehyde may be effected by the following procedure: From 5 to 10 grms. of the fruit juice or, when sorbitol-free juices are present, up to 40 grms. are dissolved in 5 to 10 times the quantity of tepid water, the solution being then fermented at 25° to 27° C. With jams, fruit jellies, etc., 15 to 75 grms., mixed with 5 to 10 times as much water, are heated for 1 to 2 hours on a boiling water-bath and the resulting solution cooled and fermented. When fermentation is complete (up to 8 days), the liquid is filtered by suction through asbestos and the filtrate, if coloured, is boiled gently for 2 to 3 minutes with 3 to 7 grms. of pure animal charcoal and again filtered through either asbestos or Seitz filtering material. The clear liquid is evaporated under diminished pressure at 50° to 60° C. to a syrup, which is heated with two or three 30-ml. quantities of ethyl or methyl alcohol, this being absolute if the residue treated contains much sugar or colouring matter from the fruit. The united extracts are left for about an hour, and are then passed through a dry filter, the filtrate being evaporated, under diminished pressure and at a low temperature, to a syrup. If caramel has formed, the syrup is dissolved in water and treated with a little charcoal. The final residue is treated with 1 ml. or, if then too viscous owing to the presence of sugar or lactic acid, with a further 0·2 ml. of dilute sulphuric acid (1 : 1), and then with 0·1 ml. of benzaldehyde. If no benzylidenesorbitol crystals then separate, up to 0·1 ml. of the aldehyde is added dropwise. The mixture is then shaken—for 15 minutes if very small amounts of sorbitol are present. After standing for about 12 hours in a cold chamber, the mass is taken up in about 100 ml. of water and the extract is filtered. after an hour, through a fritted glass crucible or a hardened filter-paper on a Gooch crucible. The benzylidenesorbitol is identified by conversion into hexa-acetylsorbitol or by its colour reaction with acetone. Sorbitol is found in apples, pears, quinces, cherries, mirabels, greengages, plums, peaches, apricots, raisins, currants, sultanas, and dried dates, but not in grapes, raspberries, redcurrants, bilberries, cranberries, gooseberries, strawberries, oranges, mandarins, lemons, bananas, pineapples, figs (fresh or dried), or hips. Fruit products made from one and the same kind of fruit may contain widely varying proportions of sorbitol, the amount depending mainly on the condition as regards ripeness of the fruit used.

T. H. P.

"Soy" Oil. T. Takei. (*J. Soc. Chem. Ind. Japan*, **1934**, **37**, 356–357B.)—Soy oil, a by-product of soy-brewing, which is a dark brownish-red oil, opaque when observed in reflected light, is found floating on the surface of the soy after pressing. It is difficult to bleach and deodorise by the usual processes. Hitherto, considered as a mixture of soya and wheat oils together with some decomposition products, it is now found to consist mostly of a mixture of ethyl esters of various fatty acids, and is susceptible to refining by distillation. The constants of the oil are:—sp.gr. at 15° C., 0·89266; n_D^{20}, 1·4630; relative viscosity at 16° C., 13·155; flash-point, 76·5° C.; saponification value, 186·38; iodine value, 102 to 132 (3 samples); acid value, 39·15–45·19. The results obtained on distillation were as follows:

	Temp. °C.	Yield per cent.	Saponification value	Iodine value	Acid value
Distillation with steam	200	6	214·27	116·10	20·55
	200–220	8·5	182·30	95·90	23·89
	220–240	31·4	193·50	66·91	28·98
	240–260	26·3	188·89	78·31	61·61
	260–300	21·5	177·35	118·80	120·23
		93·7			
Distillation *in vacuo*	170–180	27·06	190·45	120·14	19·69
	180–190	27·06	185·04	131·77	22·85
	180–190	21·76	198·99	139·36	41·49
	190–195	7·35	194·25	144·88	85·22
	195	3·53	192·65	141·26	127·94
		86·76			

D. G. H.

Drying Properties of the Polymerised Products of Sardine Oil and of Methyl Esters Derived from Sardine Oil. K. Kino. (*J. Soc. Chem. Ind. Japan*, **1934**, **37**, 439–442B.)—Twelve 700-ml. samples of sardine oil and of the methyl esters of the highly unsaturated fatty acids and of the liquid fatty acids were heated at 290 to 300° C. in an atmosphere of hydrogen, and at suitable intervals 30-ml. samples of the polymerised products were withdrawn. The samples from the methyl esters were distilled under reduced pressure (3 mm.), the iodine values and molecular weights of all the fractions were determined, and drying tests were made. During the first hour the iodine values of the polymerised esters decreased rapidly, but the molecular weights of distillation residues increased to nearly twice those of the original esters, thus confirming a preferential intramolecular reaction between two double bonds in one molecule of methyl esters of highly unsaturated acids. Distillation residues taken after 5 hours' treatment dried after 7 or 8 days at 30° C., but those taken after still further treatment took much longer to dry. The acetone-insoluble products from the polymerised oils did not change in appearance in 2 months, nor did the polymerised oils themselves.

D. G. H.

Fatty Substances of Shell Fish, Oyster, etc. M. Tsujimoto and H. Koyanagi. (*J. Soc. Chem. Ind. Japan*, **1934**, **37**, **436–439B**.)—The fatty substance present in the oyster (*Ostrea gigas*), onagai (*Mya arenaria*), ezohibari (*Volsella modiolus*), akanishi (*Rapana thomasiana*), and ushinotsume (*Cellana nigrolineata*) was found to contain in each case the peculiar sterol previously found by the authors in other shell fish, and giving a characteristic red colour reaction when a drop of sulphuric is added to 5 mgrms. of the sample dissolved in 3 ml. of acetic anhydride. This substance, now called conchasterol, was obtained in a pure state from hamaguri by dissolving 1 grm. in 100 ml. of methanol, and repeatedly recrystallising the crystals from about 100 times as much solvent. The m.pt. is 133 to 134° C., and the m.pt. of the acetyl compound after 4 recrystallisations from alcohol, 144·5 to 145·5° C. Conchasterol was also found in tarabagani liver (*Paralithodes Crustacea*), and in calamary (*Cephalopod*) oils, but is absent from fish body and liver oils, and from whale blubber and liver oil. D. G. H.

Formation of Isomeric Unsaturated Fatty Acids in the Hydrogenation of Oils. S. Ueno. (*J. Soc. Ind. Japan*, 1934, **37**, 457–458B.)—Japanese sardine oil was hydrogenated at high temperatures (250–300° C.) with large proportions of catalyst (up to 10 per cent. of nickel) at ordinary pressure, hydrogenation being stopped when the m.pt. of the oil was approximately 40° C. The oil was then filtered, saponified and decomposed with mineral acid, and the solid fatty acids were separated by the lead salt and alcohol method. The amount of *iso*-oleic acid was then calculated from the iodine value. It was found that under these conditions the yield of *iso*-oleic acid was diminished. The quantity of catalyst used bore no relation to the formation of the *iso* acid, and at temperatures above 275° C. the formation ratios were much more irregular than at 250° C., presumably owing to polymerisation and decomposition. D. G. H.

Colorimetric Determination of Chlorogenic and Caffeic Acids in Roasted Coffee. W. Plücker and W. Keilholz. (*Z. Unt. Lebensm.*, 1934, **68**, 97–109.)—Roasted coffee is found to contain an ingredient which disturbs the determination of chlorogenic acid by Hoepfner's colorimetric method (ANALYST, 1933, 58, 100, 702). Detailed examination of the procedure of this method shows that the intensity of the colour produced is greatly influenced by the quantities of the reagents added. This influence may be markedly diminished by adding an acetate buffer solution in place of the acetic acid. The following modified method is hence suggested: 10 ml. of the chlorogenic acid solution are treated in a test-tube with 0·3 ml. of a solution containing 10 ml. of glacial acetic acid and 30 grms. of sodium hydroxide in 100 ml. of water. The liquid is cooled to 8° C., treated with 0·3 ml. of 40 per cent. sodium nitrite solution, kept at exactly 8° C. for 3 minutes, and afterwards treated with 0·3 ml. of 10 per cent. sodium hydroxide solution. The transparency of a 1-cm. layer of the solution is then determined by means of a step-photometer. A table is given showing the values of the transparency towards different light filters for solutions of chlorogenic acid of different concentrations.

Details are given of the procedure to be followed in applying this method to the determination of chlorogenic acid in raw coffee. The results obtained with a number of samples agree well with those given by Hoepfner's method. A further method is described, in which the chlorogenic acid is converted, by treatment with potassium hydroxide, into caffeic acid (ANALYST, 1933, 58, 701). This is then treated with sodium nitrite, and the colour intensity is measured photometrically.

T. H. P.

U.S.P. Test for Soluble Alkalis and Alkalinity in Milk of Magnesia and Magnesium Oxide. H. Wales. (*J.A.O.A.C.*, 1934, **17**, 536–539.)—In order to ascertain the end-point for the assay of milk of magnesia and magnesium oxide, solutions of magnesium sulphate and magnesium chloride containing acid in slight excess were titrated potentiometrically with sodium hydroxide solution. The end-points, characterised by sharp breaks in the curves, lie between p_H 4 and 8. As the transition intervals for methyl orange and phenolphthalein are, respectively, p_H = 3·1 to 4·4 and 8·2 to 10·0, neither of these indicators is applicable. Methyl red, with transition interval at p_H = 4·2 to 6·3, is, however, suitable.

To test for soluble alkalis in milk of magnesia, the Revision Committee for U.S.P. XI suggests the following procedure:—Twenty ml. are diluted to 200 ml. with distilled water and filtered, 50 ml. of the filtrate being titrated with 0·1 *N* sulphuric acid in presence of methyl red; not more than 0·4 ml. should be required. Eight samples of commercial milk of magnesia gave results ranging from 0·25 to 0·80 ml. and three laboratory preparations 0·33 to 0·35. The titrations were followed potentiometrically, all the curves thus obtained showing a change in slope at p_H = about 6, owing to presence of carbonate. Products more alkaline than magnesium hydroxide were not present in more than negligible amount. There is no connection between the p_H value of the solution of the milk and the result of the titration for soluble alkalis.

T. H. P.

Differentiation between Light and Heavy Magnesium Oxide. H. Wales and G. L. Keenan. (*J.A.O.A.C.*, 1934, **17**, 534–536.)—The Revision Committee of U.S.P. XI proposes the following test to distinguish between light and heavy grades of magnesium oxide: "Place 1 grm. of magnesium oxide, previously sifted through a No. 100 sieve, in a 50-ml. graduated cylinder provided with a glass stopper. . . . Add distilled water until a volume of 50 ml. is obtained. Agitate the mixture for exactly one minute and set it aside for sedimentation. Within fifteen minutes the column of magnesium oxide measures not less than 30 ml. in case of the light oxide and not more than 5 ml. in case of the heavy oxide." The results of an examination of eight samples made by three manufacturers show that this proposed test cannot be depended on to distinguish between the two grades.

A better criterion is afforded by a weight-bulk relation, determined by measuring the volume occupied in a graduated cylinder by a definite weight of the oxide (*cf.* Liverseege, Bagnall and Lerrigo, *Pharm. J.*, 1926, **117**, 146), but the procedure must be accurately standardised if consistent results are to be obtained. Microscopic examination appears to be a still more promising means of differentiation.

T. H. P.

Biochemical

Role of Copper in Carbohydrate Metabolism. H. L. Keil and V. E. Nelson. (*J. Biol. Chem.*, 1934, **106**, 343–349.)—The oral administration of copper alone to anaemic rats produced a type of glucose tolerance curve different from that obtained with the same animal before the ingestion of the mineral. A significant lowering of the maximum point demonstrates a role of copper in nutrition apart from that of haemoglobin formation. Since the haemoglobin values were unaltered, the effect was not due to ordinary physiological oxidative processes, but must have arisen from some hitherto undescribed property of copper. Sugar tolerance tests showed that pure iron alone does not improve the glucose utilisation. An increase of haemoglobin in anaemic rats produces a proportional increase in sugar tolerance, together with a lowered glucose level in the blood after a 24-hour fast. Animals suffering from nutritional anaemia give higher blood-sugar values after 24 hours of fasting than are obtained with normal controls of the same age, and this is independent of sex. S. G. S.

Preparation of Sodium Tungstate Free from Molybdate, together with a simplified Process for the Preparation of a Correct Uric Acid Reagent. O. Folin. (*J. Biol. Chem.*, 1934, **106**, 311–314.)—The molybdates are converted into sulphomolybdates which are soluble in alcohol and water and can be easily separated from the alcohol-insoluble tungstate. The sodium tungstate (1000 grms.) is dissolved in 2000 ml. of water, and dilute hydrochloric acid (1 : 1) is added slowly, with stirring, until the solution is neutral to litmus paper. The liquid is then transferred to a large flask and hydrogen sulphide is passed into it, in a moderately rapid stream, for 15 to 20 minutes, after which the flask is then stoppered and allowed to stand overnight. After standing, the solution is transferred to large beakers, and to it is added, very slowly at first, and with constant stirring, about two-thirds of its volume of alcohol. The paratungstate is precipitated, and the coloured sulphomolybdates remain in solution. The mixture is allowed to stand until the next day, when it is filtered by decantation on a large Buchner funnel, and the residue is washed with 50 per cent. alcohol until the filtrate is colourless. The precipitate is then transferred to a 4-litre beaker, 1·5 litre of water and about 2 ml. of bromine are added, and the whole is stirred for a few minutes, and then heated over a burner, the stirring being continued until all the surplus bromine has been removed. The heating is continued, and clear, saturated sodium hydroxide solution is added until the solution gives a permanent and fairly strong reaction to phenolphthalein paper. The solution is then cooled and filtered, if necessary, the tungstate is precipitated with alcohol as before, and the precipitate is dried. The sodium tungstate thus obtained gives a moderate, permanently alkaline reaction to phenolphthalein, its solutions are clear, and it does not give the slightest trace of pink colour in the potassium xanthate test for molybdate described by Folin and Trimble (*J. Biol. Chem.*, **1924**, **60**, **474**).

The uric acid reagent may be prepared by placing 100 grms. of the sodium tungstate in a 500-ml. Florence flask. From 32 to 33 ml. of 85 per cent. phosphoric acid are mixed with 150 ml. of water, and this solution is poured on to the tungstate and mixed. A few pebbles are added, and the solution is boiled very gently over a micro-burner for 1 hour. Loss of liquid is prevented by using, as a condenser, a funnel holding a 200-ml. flask filled with cold water. After boiling, the solution is decolorised with bromine water and the excess of bromine is boiled off. The solution is then cooled and diluted to 500 ml. If the reagent so obtained gives a blank with urea cyanide, with or without tyrosine, 3 to 5 grms. more of sodium tungstate are added, and the solution boiled for 10 to 15 minutes, cooled and decolorised as before. S. G. S.

Insulin-Content of the Pancreas in Cattle of Various Ages. A. M. Fisher and D. A. Scott. (*J. Biol. Chem.*, 1934, **106**, 305–310.)—The amount of insulin which can be extracted per grm. of beef pancreas has been found to vary with the age of the animal. Foetal beef pancreas is relatively rich in this hormone. In cows of over 7 years of age pregnancy does not appear to affect the insulin-content of the pancreas. The amounts found varied from 33 international units per grm. for foetal calves under 5 months old, to 2 international units per grm. for cows of over 7 years old, the decrease being progressive with increasing age. S. G. S.

Further Investigations on the New Vitamin *B* Growth-promoting Factor for Rats, found in Whole Wheat. N. Halliday. (*J. Biol. Chem.*, 1934, **106**, 29–40.)—Bran is a fairly good, but wheat germ is the richest source of this new vitamin factor. It may be extracted with dilute acid or dilute alcohol, but not with ether. By the use of a method similar to that described by Peters and his colleagues (*Biochem. J.*, 1933, **27**, 225, and *Nature*, 1933, **131**, 617) it has been possible to prepare a crystalline concentrate. In many respects this is very similar to vitamin B_4, but the differences are too great to warrant a definite conclusion. S. G. S.

Effects of Ascorbic Acid (Vitamin *C*) on Toxins. E. Harde. (*Compt. rend.*, 1934, **199**, 618–620.)—Mice, which are more resistant to certain infections than guinea-pigs, are capable of synthesising large amounts of ascorbic acid in their bodies. These animals thrive on diets which would be scorbutic to guinea-pigs. It is already known that ascorbic acid has the power of neutralising diphtheria toxin, both *in vitro* and *in vivo*, and this is associated with the disappearance of ascorbic acid now discovered in the cortex of the suprarenal glands, either of guinea-pigs which have died from diphtheria or of mice which have died from *B. typhi murium* infection. The silver nitrate method, described by Szent-Györgyi (*Biochem. J.*, 1933, **22**, 1387), was used for these experiments. It was also found that when guinea-pigs were given an injection of a toxin, followed by injections of ascorbic acid, although induration and sloughing may occur at the site of injection, yet the animals survived. It is suggested that ascorbic acid has marked protective powers, especially in infections and intoxications which give lesions in the cortex of the suprarenal glands and in the gastro-intestinal tract. S. G. S.

Vitamin *C* Content of Human Tissues. M. Yavorsky, P. Almaden and C. G. King. (*J. Biol. Chem.*, 1934, **106**, 525–529.)—Human tissues from hospital autopsies were examined for vitamin *C* within twenty-four hours of death. The determinations were carried out by titrating a trichloroacetic acid (8 to 10 per cent.)

extract of the tissue with 2, 6-dichlorophenolindophenol. The results corresponded with the figures obtained for guinea-pig tissues, and suggest that latent human scurvy is fairly common. Arranged in descending order of their vitamin *C* contents, the various tissues are:—adrenal glands, brains, pancreas, liver, spleen, kidney, lung, heart, muscle. Below the age of ten years, the thymus has a value as high as that for the pancreas. The average values ranged from 0·55 mgrm. per grm. for the adrenals to 0·04 mgrm. per grm. for the heart, but individuals varied as much as from three times down to one-tenth of the average value. S. G. S.

Bacteriological

Bacillus Tuberculosis in Butter. J. W. Edington. (*Lancet*, 1934, ii, 81.)—Some of the technical difficulties met with in carrying out the biological test for the presence of *B. tuberculosis* in butter may be avoided by the following process: From 60 to 100 grms. of butter are melted at 40° C. in 150 ml. of distilled water in a beaker. This is then pumped twice through a cream-making machine into a centrifuge tube, and the solution is centrifuged at 3000 r.p.m. for 30 minutes. The cream is removed with the aid of a stout wire, the supernatant liquid is poured off, and the deposit is suspended in 5 ml. of saline solution. This solution is then inoculated subcutaneously in equal amounts in the antero-internal aspects of the right thigh of each of two guinea-pigs, the inguinal glands having been previously squeezed according to the method of Bloch (*Berl. klin. Woch.*, 1907, **44**, 511). After one month the animals are killed and examined carefully for the presence of tuberculosis arising from the site of inoculation. The examination of 15 samples of Danish and 25 samples of New Zealand and Australian butters revealed the presence of *B. tuberculosis* in one sample of Danish origin. Since all these butters are usually believed to be made from pasteurised cream, the finding of a sample containing this organism is disconcerting. S. G. S.

Orthophenylphenol as an Antiseptic. H. C. Fuller. (*Ind. Eng. Chem.*, 1934, **26**, 946.)—Orthophenylphenol and its derivatives have a high antiseptic value and are relatively non-toxic to animals. The compounds also have definite penetrating powers, and can be used, not only for their own effect, but also to bring about the penetration of other chemicals that ordinarily do not exert their effects beyond the surface of the skin. It has been found useful in this respect in salves, ointments and sprays for treating colds, rheumatic conditions and muscular aches, and also in throat tablets and gargles. In addition, it is well tolerated by children. The soluble sodium salt, dissolved in physiological salt solution, was used for intravenous injection in *Streptococcal* and *Staphylococcal* infections, and showed a definite curative effect without any injury to animal or human patients.
S. G. S.

Examination of Soils by Means of Aspergillus Niger. A. M. Smith and A. Dryburgh. (*J. Soc. Chem. Ind.*, 1934, **53**, 250–254T.)—Since the *Aspergillus* method for soil examination is cheap and speedy, the more important factors concerned in the laboratory technique have been examined. It was found that considerable latitude in the concentration of inoculum employed is allowable;

that ammonium nitrate or sulphate is better than citrate as a supply of nitrogen, and that the vessels used should not vary in diameter by more than a few mm., since area of growth is a much more important factor than actual amount of suspension. For the determination of "available potash," 2·5 grms. of soil are placed in a bottle of 130 ml. capacity, with diameter 5·5 cm.; and 30 ml. of nutrient solution are added [sucrose, 10; citric acid, 1; peptone, 0·1; P_2O_5 (as ammonium dihydrogen phosphate), 0·075; ammonium nitrate, 0·36; magnesium sulphate, 0·03; copper, 0·00015; iron, 0·0001; and zinc (all as sulphates), 0·0001 per cent.] A few drops of conidia suspension are added, the mixture is incubated for 6 days at 35° C., the mycelium is removed with forceps, washed, dried overnight at 50 to 60° C., then for 2 hours at 60 to 100° C., finally for 2 hours at 100° to 105° C., and cooled and weighed. The same procedure is followed for "available phosphate," except that 5 grms. of soil are taken and the nutrient solution contains 0·02 per cent. of K_2O as potassium sulphate and no phosphate. In routine work the experiments are carried out in quadruplicate and 4 mycelia are weighed together, and the average weight is taken. The cultures are prepared on slopes of agar containing 1 per cent. of glucose, 0·1 per cent. of asparagine, and 0·05 per cent. of dipotassium hydrogen phosphate in tap water. A small quantity of conidia is taken from the slope with a moist wire-loop and shaken up with a few ml. of distilled water, and 3 drops of the suspension are used. In working with 7 soils and 3 strains of organism, strain was found to have a specific effect in the determination of potassium, and there was a distinct interaction between soil and strain. Since sufficient acid must be present in the soil-culture solution suspension to prevent growth of various soil micro-organisms, the initial reaction of a soil may have little influence on the final p_H value of suspension. Experiments were made with an infertile sandy loam treated with increasing amounts of calcium hydroxide in 1931, and on a normal clay loam, one sample of which had been treated with calcium hydroxide since 1930 to decrease acidity, and the other with sulphur to increase acidity. Seventy pots of soil were treated, and it is concluded that whatever effect excess of calcium carbonate in the soil may have on the fungus development, normal application of lime to correct soil acidity would not exert any practical influence. In comparing the Mitscherlich and *Aspergillus* methods for 40 soils, the correlation coefficient was 0·77 for the phosphate figures, but only 0·40 for the potassium figures. That the *Aspergillus* method is not so sensitive as the other common methods, such as those of Mitscherlich or Neubauer or extraction methods, may be partly due to the fact that the mycelium weight is not a direct measure of the nutrient uptake, since the composition of the mycelium varies irregularly, and its analysis is impracticable. There seems little doubt that the decisive factor in the growth of the organism is the nutrient content of the soil, and the behaviour of *Aspergillus* certainly seems to be sufficiently constant to enable the soils to be placed into 2 or 3 large groups according to their fertiliser requirements. The occurrence of border-line cases is common to any method of estimating soil fertility, but it will be necessary to examine a greater variety of soil types from suitable field experiments, in order to establish the reliability of the *Aspergillus* method.

D. G. H.

Water Analysis

Removal of Iron and Manganese from Water. S. B. Applebaum and M. E. Bretschger. (*Ind. Eng. Chem.*, 1934, **26**, 925–931.)—Iron and manganese in water supplies, in amounts greater than 0·3 to 0·5 p.p.m., may cause an unpleasant taste, unsightly stains and troublesome deposits, affecting both domestic and industrial use. In general, iron and manganese may be removed by two methods. The first is by oxidation to the higher oxides and hydroxides, which are insoluble and can be removed by filtration. The second method is by base exchange through zeolite without oxidation. The oxidation reactions are interfered with by a number of factors, such as the presence of free carbon dioxide, low total solids, low p_H value and organic matter. The various types of iron and manganese removal methods consist of (i) a simple form of aeration followed by filtration, (ii) more thorough aeration for removal of free carbon dioxide, followed by filtration, (iii) aeration, followed by basin settling and final filtration, (iv) aeration, liming, basin settling and filtration, (v) similar to (iv), but using special coagulants such as aluminium compounds, potassium permanganate, and chlorinated copperas, together with an adjustment of the p_H value, (vi) oxidation and filtration through manganese zeolite, (vii) filtration through sodium zeolite without oxidation. The authors suggest that, for any given water supply and set of engineering conditions, experimental studies should be made, both in the laboratory and in the field, in order to determine the optimum conditions of working.

S. G. S.

Removal of Fluorides from Drinking Water. R. H. McKee and W. S. Johnston. (*Ind. Eng. Chem.*, 1934, **26**, 849–851.)—The presence of fluorine in drinking water to the extent of 5 to 17 parts per million is known to be the cause of mottled enamel on teeth. Adsorption by carbon removes fluorides from potable waters, but some carbons are much less efficient than others. The most satisfactory results are obtained with a carbon which is a residue discarded by the soda pulp industry, but, even with this, there is no removal of fluoride until the p_H value of the water has been reduced to about 3. Attempts to reduce the fluorine to less than 1 part per million have been unsuccessful. W. P. S.

Organic Analysis

Analytical Uses of 2-Propanol. G. W. Ferner and M. G. Mellon. (*Ind. Eng. Chem., Anal. Ed.*, 1934, **6**, 345–348.)—Owing to the close similarity in physical properties, *iso*-propyl may be used instead of ethyl alcohol for many purposes in analytical chemistry, as, for instance, the following:—(i) As solvent for reagents like dimethylglyoxime, hydroxyquinoline; (ii) to reduce the solubility of a precipitate such as calcium sulphate (where this is permissible with ethanol); (iii) to effect separations, *e.g.* the separation of sodium chloride from magnesium chloride according to the method of Hillebrand and Lundell, "Applied Inorganic Analysis," or in the separation of calcium from barium by extraction of the nitrate with alcohol and ether; (iv) to wash precipitates in order to hasten drying, *e.g.* lead sulphate, nickel glyoxime (a list of 16 precipitates is given). 2-Propanol may not be used in place of ethanol for the flame test for borates or for the acetate tests of the U.S. Pharmacopoeia. The turmeric test for boric acid is less sensitive when 2-propanol is used. For the preparation of concentrated alcoholic potash solution, anhydrous 2-propanol is necessary, as in presence of water the alcohol is "salted-out" to some extent. S. G. C.

Haloform Reaction. XIV. Improved Iodoform Test. R. C. Fuson and C. W. Tullock. (*J. Amer. Chem. Soc.*, 1934, **56**, 1638–1640.)—The following procedure, which is applicable to substances which are insoluble in water, is stated to be more reliable than that in present use. The sample (0·1 ml. of liquid or 0·1 grm. of solid) is dissolved in 5 ml. of dioxan in a test-tube (diameter 150 mm.), and 1 ml. of a 10 per cent. solution of sodium hydroxide is added, followed by sufficient of a solution containing 100 grms. of iodine and 200 grms. of potassium iodide in 800 ml. of water, to produce a definite dark colour (indicating an excess) which does not disappear after 5 minutes. The mixture is heated at 60° C. for less than 2 minutes, more reagent being added with shaking, to maintain the dark colour, and the excess of iodine is removed by addition of a few drops of the sodium hydroxide solution. The test-tube is then filled with water, and after 15 minutes the precipitated iodoform is separated by filtration, and, if red in colour (owing to the presence of carbon tetraiodide), it is suspended in 3 ml. of dioxan and 1 ml. of the sodium hydroxide solution is added. When the mixture has become lemon-yellow, it is again diluted and filtered, and the m.pt. of the iodoform (119° to 121° C.) is determined. Application of the test to 96 compounds (including alcohols, acids and their derivatives, aliphatic unsaturated and mixed ketones and diketones) indicated that it is positive for compounds which contain the grouping CH_3CO-, CH_2ICO- or CHI_2CO-, joined to a hydrogen or carbon atom which is not linked to hydrogen atoms or to a group associated with powerful steric hindrance. It is also positive for compounds which decompose to give the above groupings, and negative in cases where these groupings are hydrolysed by the reagent before iodination. Benzoyl acetone and certain nitro- and amino-compounds show a premature appearance of a brown colour, and the true colour does not appear until the end of the reaction. The mechanism of the reaction is explained by the three-fold effect of the reagent, *viz.* oxidation of alcohols or amines, replacement of active hydrogen atoms, and cleavage of carbon chains (*cf.* Woodward and Fuson, *id.*, 1933, **55**, 3472), and this explanation is discussed for individual cases.

J. G.

Identification of Amines as 2, 4-Dinitrobenzoates. C. A. Buehler and J. D. Calfee. (*Ind. Eng. Chem., Anal. Ed.*, 1934, **6**, 351–352.)—2, 4-Dinitrobenzoic acid combines with a wide variety of aromatic and aliphatic amines, and the salts formed may be readily purified for identification purposes. The 2, 4-dinitrobenzoates of some 38 common amines have been prepared, and the melting-points are tabulated in the paper together with the melting-points of the corresponding 3, 5-dinitrobenzoates. The method of preparation of 2, 4-dinitrobenzoic acid is also described. S. G. C.

Properties of Adipoïne, a Cyclic Sugar. G. P. G. Moeys and N. Schoorl. (*Pharm. Weekblad*, 1934, **71**, 1026–1029.)—Adipoïne (α-hydroxy-*cyclo*hexanone) was prepared (*cf.* Kötz and Grethe, *J. prakt. Chem.*, 1906, **80**, 487) by the chlorination of α-*cyclo*hexanone, and treatment of the resulting compound with potassium carbonate. The recrystallised adipoïne melted at 91° C. (*cf.* Bergmann and Gierth, *Ann.*, 1926, **448**, 48), and was very volatile in steam; its solubility in water was 1:1750; in absolute alcohol, 1:400; and in ether, 1:1000. The evidence that it is a typical sugar is based on the analytical criteria of Milius and Schoorl (*Pharm. Weekblad*, 1916, **53**, 1249), *viz.* (1) A cupric salt is reduced to cuprous oxide in the cold in the presence of sodium hydroxide solution (Trommer reaction). (2) Osazones were prepared (after Denigès) and the m.pts. after recrystallisation were determined (osazone from phenylhydrazine, 152 to 153° C.; *p*-bromophenyl-osazone, 183 to 185° C.; *p*-nitrophenyl-osazone, 236 to 237° C.). (iii) In Rose's reaction (*Z. anal. Chem.*, 1931, **87**, 110), which is said to be specific for "open" sugars, a purple colour is produced on warming a solution of the sample with 2 *N* sodium carbonate solution and a drop of an alcoholic solution of *o*-dinitrobenzene, and this gave a positive result with a 1 : 2000 solution of adipoïne. (iv) The mean ratio of the rates of reduction of Luff's and Fehling's solutions was determined on 10 to 50 mgrms. of adipoïne, with 25 and 20 ml. of reagent, heated for 10 and 2 minutes, respectively; since 1·35 and 0·82 atoms of oxygen per molecule of adipoïne were involved, respectively, the ratio is 1·65 : 1, which is a normal value for sugars. Evidence of the *cyclo*-hydroxy-desmotropic change on reduction suggested by Bergmann and Gierth (*loc. cit.*) was also obtained. J. G.

Studies on the Merino Fleece. II. Separation of Cholesterol and "*Isocholesterol*" of Wool Wax. M. R. Freney. (*J. Soc. Chem. Ind.*, 1934, **53**, 289–291T. *Cf.* ANALYST, 1934, **59**, 500.)—The Twsett method of chromatographic adsorption has been applied to the colourless sterols of wool wax. The adsorbing medium used was alumina in the form of a column, 2·5 cm. in diameter and 16 cm. long, and the 2·5 grms. of crude unsaponifiable matter of wool wax (obtained by ethereal saponification in the cold, and having m.pt. 45° C., and $[\alpha]_D + 1°$) was dissolved in 100 ml. of hot solvent (benzene 40, and petroleum spirit 60 per cent.), and drawn by suction slowly through this column, which was first wetted with solvent. The column was subsequently washed with 200 ml. of hot solvent, and the alumina was pushed out and divided into 5 lengths or fractions. Each of these was extracted with 150 ml. of boiling solvent (methyl alcohol 80, and benzene 20 per cent.), which was then decanted, filtered and evaporated to 10 to 20 ml. Any white crystals which separated overnight were filtered off and washed with methyl alcohol, and the filtrate was evaporated to dryness. The crystals were heated with acetic anhydride, and the acetates were crystallised and washed with methyl alcohol. A recovery of over 85 per cent. of the original material was made. Fractions 1 and 2 (from the top of the column) gave no crystals under the conditions described. Those obtained from fraction (3) differed only slightly from cholesteryl acetate, whilst fraction (5) yielded crystals approximating closely to those of *iso*cholesteryl acetate, and these comprised the bulk of the fraction. Cholesterol and *iso*cholesterol may therefore be separated with comparative ease from wool wax. A sample of very crude *iso*cholesterol, and also a purer sample were subjected to similar treatment, but a separation of lanosterol and agnosterol could not be effected. D. G. H.

Determination of Strong Acid and of Buffer Salts in Vegetable-tanned Leather. R. F. Innes. (*J. Inter. Soc. Leather Trades Chem.*, 1934, **18**, 457–464.)—The basis of the present work is that of Richardson (*Proc. Roy. Soc.*, 1934, **115** [B], 170), who found that if acids are made up in 90 per cent. acetone solution, the ionisation of weak organic acids (of p_H 3 or over) is almost completely suppressed; that of stronger organic acids of p_H less than 3 (*e.g.* citric, tartaric, oxalic) is almost suppressed, but that of "true strong acids" is not greatly affected. Thus hydrochloric acid in admixture with oxalic acid may be titrated alone by using a suitable indicator. With sulphuric acid it is not quite so simple, owing to its second ionisation in 90 per cent. acetone, giving a p_H value by titration of about 3·3. These facts may be applied to a determination of strong acids in the leather by placing a convenient weight of leather (say 10 grms.) in an 8-cm. filter funnel to the stem of which is fixed a piece of rubber tubing and clamp. A piece of broken porcelain at the bottom of the funnel prevents entry of fragments of leather into the tube. The leather is covered with water, which is left standing overnight, after which it is withdrawn through the tube and the process repeated several times, 20 minutes' contact being allowed each time. One hundred ml. of extract are collected, and, after mixing, 5 ml. are taken for titration after addition of 45 ml. of acetone. If the p_H value is less than 3·4, strong acid is present, and 0·02 *N* sodium hydroxide solution will give a measure of the acidity; a second extraction is then desirable. If the p_H is 3·4, a trace of strong acid is present, and if it is sulphuric acid, cannot exceed 0·004 *N* in the undiluted extract or 0·2 per cent. on the leather. If the p_H is over 3·4 and under 4·0, the equivalent of sulphuric acid present is less than 0·1 per cent. on the leather. If the initial p_H value is over 4·0, strong acid is absent, and titration with 0·02 *N* alcoholic hydrochloric acid will give a measure of the amount of buffer salt present. The method was successfully applied to Nigerian-dyed leather, English-dyed leather containing "protective agent," and sumach-tanned crust leather, all of which showed the presence of salts of organic acids, whilst English-dyed and mimosa crust leather had only a trace. It is suggested that a leather should be regarded as free from strong acid only when the p_H value of its aqueous extract in the proportion of 1 grm. per 10 ml. (when mixed with acetone to a concentration of 90 per cent. acetone) is 4·0 or over, and that no tolerance figure be allowed. D. G. H.

Determination of Total Sulphur in Keratins. J. Barritt. (*J. Soc. Chem. Ind.*, 1934, **53**, 291–294T.)—*Wet Oxidation.*—The Mackay methods (*id.*, 1930, **49**, 233, 401T) were investigated, but it was found difficult to obtain reproducible results having the required degree of accuracy. Samples (0·8 grm.) were, therefore, hydrolysed for 2 to 4 hours with 20 ml. of 20 per cent. hydrochloric acid, and the Benedict–Denis method, as modified by Rimington (*id.*, 1930, **49**, 139T), was applied, the barium sulphate being dried in a small Gooch crucible at 140° C. Samples were also boiled under a reflux condenser for 1 to 2 hours with 20 ml. of concentrated nitric acid, the solution being then diluted to 50 ml. and

20 ml. taken for the determination. In both cases the variations from the means were of the same order, but the latter method (and also the Carius method) gave slightly higher results (by about 0·13 per cent.), indicating a loss of volatile sulphur (*e.g.* as hydrogen sulphide) on boiling with hydrochloric acid (*cf. infra*). *Dry Oxidation.*—A bomb designed for the determination of sulphur in coal (*cf.* Farrar and King, *J. Text. Inst.*, 1926, **17**, 588T) has been modified for the present purpose, and consists of a mild steel cartridge (8 × 2·3 cm.) 2 to 3 mm. thick, which fits into an outer steel case. Samples (less than 0·5 grm.) are mixed with sodium peroxide with steel forceps, and are filled into the cartridge so that the layers of mixture are between layers of peroxide, the lid being clamped on when the bomb is three-fourths full. The bomb is then heated in an inclined position for 10 minutes, after which it is cooled, and the contents are leached out and made just acid with hydrochloric acid. Iron is removed with ammonia, and the sulphates in the filtrate are precipitated. The results are in close agreement with the nitric acid method (*i.e.* 3·73 per cent. of sulphur on the dry weight). In all cases the wool is first pulled out, degreased with benzene at 60° C., dried, washed in 6 changes of distilled water, air-dried, and finally conditioned for several days. The experiment of Hoffman and Gortner (*J. Amer. Chem. Soc.*, 1922, **44**, 341) on the hydrolysis of cystine by 20 per cent. hydrochloric acid was repeated, the gases being carried over into a solution of cadmium acetate. The results indicate that a very small amount of volatile sulphur compounds is obtained, although small quantities of hydrogen sulphide were detectable when wool was added, and this could not be fixed by the further addition of salts which form insoluble sulphides. Since similar results are obtained on the hydrolysis of casein, which is rich in methionine, the only sulphur-containing compound other than cystine so far isolated from wool (about 0·5 per cent. present), the low results obtained by the hydrochloric acid method (*supra*) remain unexplained. J. G.

Inorganic Analysis

Detection and Determination of small Quantities of Bromine. J. Frezouls. (*Ann. Falsificat.*, 1934, **27**, 351–357.)—The proposed method is a modification of that of Denigès and Chelle, *i.e.* liberation of the element by means of chromic acid in presence of fuchsin-sulphuric acid reagent (*Ann. Chim. anal.*, 1913, 11; 1918, 81; *J. Soc. Chem. Ind.*, 1913, **32**, 141; 1918, **37**, 284A). The oxidiser recommended by the author is a solution of 1 grm. of ammonium persulphate in 10 ml. of cold strong sulphuric acid. The solution keeps for about a fortnight if stored in the dark. Ten ml. of the solution to be tested (maximum bromine-content, 0·01 grm.) are treated with a drop of hydrochloric acid if free from chloride, 2 ml. of fuchsin reagent, 3 drops of oxidiser, and 1 ml. of chloroform, and the tube is shaken repeatedly; the chloroform layer becomes reddish-violet. The fuchsin reagent should be quite colourless, which is brought about by agitation with infusorial earth (treated with dilute sulphuric acid, washed, and dried) and filtration. The reaction may be used for the colorimetric determination of bromine; with the above quantities the sensitiveness is 0·005 mgrm. W. R. S.

New Colour Reaction of Ammonia. L. Lapin and W. Hein. (*Z. anal. Chem.*, 1934, **98**, 236–240.)—The reaction is based on the appearance of a blue colour when a solution containing ammonium salt is shaken with hypobromite and thymol. The reagents are: a 25 per cent. solution of thymol in alcohol, and sodium hypobromite freshly prepared from 1 volume of 2 *N* sodium hydroxide solution, and 2 volumes of saturated bromine water. The liquid to be tested (5 ml.) is first mixed in a wide test-tube with 1 ml. of thymol solution, then with 12 to 15 ml. of hypobromite solution, and, after one to two minutes, with 5 ml. of ether or xylene. The liquid is cautiously mixed by inverting the tube several times, when the coloured compound dissolves in the solvent. The sensitiveness is 0·01 mgrm. of ammonia per 100 ml., *i.e.* one-fifth of that of Nessler's reaction. The only interfering metals are lead and platinum, which cause a brownish tint in the ethereal layer; the interference of lead is counteracted by addition of sulphate. Sulphide ion requires an excess of hypobromite. Hydroxylamine and hydrazine salts, as well as hydrogen peroxide, weaken the intensity of the colour. Organic compounds do not interfere, with the exception of aniline, which imparts a yellowish-pink tint to the ether. W. R. S.

Colorimetric Standards for Silica. H. W. Swank and M. G. Mellon. (*Ind. Eng. Chem., Anal. Ed.*, 1934, **6**, 348–350.)—In various methods in which the yellow silicomolybdic acid is determined colorimetrically, permanent colour standards of picric acid (King and Lucas, *J. Amer. Chem. Soc.*, 1928, **50**, 2395) or potassium chromate (Amer. Public Health Assoc., "Standard Methods of Water Analysis," 1933, p. 66) have been adopted. As a result of a study of the comparison of the coloured silicomolybdic acid solution with these standards with the aid of visual and photo-electric colorimeters, Nessler tubes, and a spectrophotometer, it was concluded that these permanent colour standards do not reproduce the colour of the silica solution sufficiently satisfactorily. It was found, however, that a solution of potassium chromate when suitably buffered, as with borax, gave a very good reproduction of the silica colour. The following table gives the concentration of buffered potassium chromate and silica for equivalent colour:

Potassium chromate[1] ml.	Silica[2] p.p.m.	Potassium chromate ml.	Silica p.p.m.
0·0	0	8·0	16
1·0	2	9·0	18
2·0	4	10·0	20
3·0	6	11·0	22
4·0	8	12·0	24
5·0	10	13·0	26
6·0	12	14·0	28
7·0	14	15·0	30

[1] 0·63 grm. of potassium chromate per litre; the volumes specified are to be diluted with 25 ml. of a 1 per cent. solution of borax and enough water to make a total of 55 ml.

[2] 50 ml. of sample solution, together with 5 ml. of reagent, as recommended in the A.P.H.A. method (see reference above).

S. G. C.

Testing China Clay. J. Grant. (*Sands, Clays and Minerals*, 1934, 2, 49–51.)—These tests have special reference to the paper and kindred industries. The moisture is determined by heating at 105° C. until the weight is constant, and should be about 10 per cent.; a figure below 7 per cent. indicates over-drying, and is frequently accompanied by a poor colour, dirt, and a high rate of settlement from suspension. Colour is assessed by comparison with a standard of a paste with water, glycerin or oil, and also after drying the paste with water; this is conveniently carried out on a white tile with wedge-shaped depressions, but the possibilities of photo-electric methods for obtaining numerical values of colour are also discussed. Foreign tinting colouring-matters can usually be detected by one of the following tests:—(i) Particles of the clay are blown on to the surface of distilled water, clear lime water and 10 per cent. hydrochloric acid, a trail of colour then being produced in one or other of the reagents behind each particle as it sinks. (ii) Since ultramarine is decolorised by acids and Prussian blue by alkalis, pastes made with the appropriate reagents will differ in shade from those made with water. (iii) A thick paste (about 25 ml.) of clay and ammonia is dried on the water-bath in a 100-ml. beaker, and any added colour then concentrates in a narrow ring on the wall of the beaker just above the surface of the clay, and may even be removed for examination; the faint brown ring frequently obtained with unadulterated clays is due to traces of organic matter, and should be neglected. (iv) China clay normally appears blue-violet in filtered ultra-violet light, but the presence of minute quantities of many tinting colours is sufficient to modify this considerably (*cf. id.*, 1933, 1, 7); examples are cited. Other loadings may also be distinguished from clay in this way. Grit is determined by washing the clay through an appropriate sieve (*e.g.* 200-mesh), and weighing the dried residue. Iron is determined by the thiocyanate reaction on an extract of the clay in boiling 10 per cent. hydrochloric acid. A test with a drop of acid under the microscope is used for calcium carbonate, and the barium chloride test for calcium sulphate should also be applied. Since plasticity and the rate of settlement are affected by the presence of traces of vegetable colloidal matter adsorbed on the clay during the washing operations, and by p_H value, weighed samples should first be boiled with water to expel air, and the cooled suspension dispersed in 0·001 N sodium hydroxide solution. A quantity of the suspension, equivalent to 10 grms. of clay, is then diluted to 100 ml. and shaken well in a cylinder, the volume of clear liquid formed during settlement being noted after various intervals of time; if desired, a curve may be plotted. Observations of the rate of disintegration of a lump of clay in water without external aid are also useful. J. G.

Microchemical

Microchemical Tests. XI. L. Rosenthaler. (*Mikrochem.*, 1933–34, 14, 363–369.)—1. *Silico-fluorides of Alkaloids.*—When solutions of the following alkaloid salts are treated with solid ammonium silico-fluoride, crystals are formed. *Quinine*: Needles. *Diocaine*: Small needles, often grouped into stars. *Codeine*: Branched groups of needles and three-cornered plates (photo-micrograph). *Pantocaine*: At first feathery crystals and rods, then tablets, mainly with irregular outlines (photo-micrograph). *Psicaine:* Flat tablets, six-sided or star-shaped. *Stovaine:* Characteristic narrow crystals, six-sided above and joined to tablets or prisms (photo-micrograph). *Strychnine:* Rods, mainly grouped together. The reaction with pantocaine may be used as a test for silicofluorides. When solid pantocaine is used the reaction proceeds in dilutions up to 1 : 1000, and is as sensitive as the reaction with sodium chloride, although less sensitive than that with barium acetate. As tests for alkaloids, the reaction with silicofluorides is useful with the local anesthetic compounds, most of which give no precipitation.

2. *Crystal Precipitation of Veramon.*—Veramon is a mixture of 1 molecule of pyramidon and 1 molecule of the compound (pyramidon + diethyl barbituric acid). Therefore reagents were tested that gave reactions with barbituric acid; of these, the Zwikker copper-pyridine reaction, and the reaction with ammonium phosphate, are positive. The reactions with lead acetate, thallium acetate, iodine and bromine are negative. With bromine only the long fine needles are formed that are obtained from pyramidon alone.

3. *Crystal Precipitation of* p-*Chlorobenzoic Acid.*—This compound is often used as a preservative. Suitable reagents are silver nitrate, mercuric acetate, uranium nitrate and aluminium nitrate, used in the solid form. The *p*-chlorobenzoic acid is best used as a solution of its calcium salt, when the use of sulphate or sulphuric acid (which would form calcium sulphate crystals) is to be avoided. *Silver nitrate:* Rods, and many-sided crystals and some small plate with irregular edges (photo-micrograph). Limit concentration:* 1 : 2500. *Mercuric acetate:* Bushes and star-like groups of needle-shaped crystals. Limit concentration: 1:2500. *Uranium nitrate:* From a 1 : 100 solution small spherical crystals are formed, and from dilute solutions (1 : 500) rods and needles, mainly in groups. Limit concentration: 1 : 2500. *Aluminium nitrate:* Groups of small needles. Limit concentration: 1 : 50,000. The 1 : 100 solutions, with the nitrates of cerium and lanthanum, give precipitates rapidly becoming crystalline. The free acid is precipitated from the sodium and calcium salts, with hydrochloric acid; for the *p*-acid the limit concentration is 1 : 2500. The appearance of the free acid is indistinguishable from that of the crystals formed with mercuric acetate, uranium nitrate and aluminium nitrate, therefore, in these cases it is probable that the free acid is also formed by hydrolysis. Free *p*-chlorobenzoic acid may also be obtained from the test substance by micro-sublimation. The small crystals obtained may be recrystallised from hot water.

4. *Reactions of Phenols in Sodium Carbonate Solution.*—Phenols alone give no precipitate with iodine in potassium iodide, but give crystalline precipitates in the presence of sodium carbonate. For the following reactions a mixture of one part of concentrated iodine solution (iodine 0·5, potassium iodide 2, water 2) and two parts of saturated sodium carbonate solution is used. With this solution most phenols give brown amorphous precipitates and a few of them crystalline precipitates. *Phenol:* Groups of needles at once, with long divided needles at the edges. *p-Chlorophenol:* Needles, mainly in groups, formed at once, some amorphous

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* As *Limit concentration* and *Limit of Identification* have been used in the translation of Emich's "*Laboratory Manual,*" these terms will be used in future in place of *Limit of dilution* and *Smallest amount recognisable.*—ABSTRACTOR.

particles. *β-Naphthol:* Interspersed among brown amorphous particles, some long colourless needles. *Hydroquinone:* Quinhydrone crystals, and, later, darker amorphous particles. The phenolic acids behave similarly to the phenols; thus salicylic acid also slowly gives groups of needles interspersed among brown amorphous grains.

5. *Crystal Precipitation of Phenolic Acids with* p-*nitroso-dimethylaniline.*—Salicylic acid, *p*-hydroxybenzoic acid, gallic acid, the three salicylic acids (*o*-, *m*-, and *p*-cresolinic acid) and α-hydroxynaphthoic acid, give crystalline precipitates with *p*-nitroso-dimethylaniline solution (0·1 grm. reagent in 5 ml. of water, 0·1 grm. sodium acetate, and filtered). The crystals formed are similar in each case, usually rods or prisms, and can be distinguished only by cryoscopic measurement. Only hydroxybenzoic acid is different, as it gives four-cornered plates.

6. *Crystal Precipitation of* Iso-*propyl-antipyrine.*—*Iso*-propyl-antipyrine is a crystalline powder, melting at 99° C., and is a constituent of the tablets "Saridol." The following are the reactions of the solution in dilute hydrochloric acid with the following reagents:—*Potassium dichromate:* Needles, rods, some forming rosettes (photo-micrograph). *Sodium perchlorate:* Similar crystals, some platelets. *Reinecke's salt* (solution): At first amorphous, then groups of five two-branched needles. [*Tetra-nitro-diamine-cobalti*] *potassium:* Branched bushes of bent thread-like crystals (photo-micrograph). *Potassium iodide:* Rods and many-sided irregular plates. The reaction with stannous chloride and potassium iodide is described below (7). The reaction with Reinecke's salt is the most sensitive; the limit concentration is 1 : 4000.

7. *Crystal Precipitation of Tin with* Iso-*propyl-antipyrine.*—A solution of the reagent in dilute hydrochloric acid on adding to a drop of stannous chloride solution rapidly gives, on stirring, colourless crystals, double pyramids, seed-shaped, and star-shaped. Bismuth and antimony do not react. The reaction is not very sensitive, as at dilutions of tin less than 1 per cent. it does not occur. The reaction can be made more sensitive (to 1 : 500) if potassium iodide is added. Dark orange rosettes of crystals are formed in an orange-violet solution. Bismuth and antimony interfere, although alone they give only amorphous precipitates with the reagent.

8. *Differentiation of Barium from Calcium and Strontium.*—When a solution of a barium salt is treated with a 5 per cent. solution of sodium 6-chloro-5-nitro-toluene sulphonate little grains are first formed, and finally long radiating needles (photo-micrograph). Calcium and strontium do not react, even in 10 per cent. solutions, but interfere when present in large amounts; a solution containing 1 per cent. of the three metals gives the barium reaction. Limit concentration (for barium alone) 1 : 2000.

9. *Crystal Precipitation of Cobalt.*—When a 1 per cent. solution of cobalt chloride is treated with a grain of potassium chromate, a brown amorphous precipitate is formed. If, however, salts of aluminium, manganese or tin are present, brown crystals are formed; the reaction is not very sensitive.

10. *A Sensitive Colour Reaction for the Alkaline Earths.*—When 1 ml. of a 1 : 10,000 solution of a salt of calcium, barium or strontium is treated with 1 ml.

of a tannin solution (1 : 1000) and two drops of $N/10$ alkali, a greenish colour is formed, and a blue-green colour or precipitate in concentrated solutions. A blank test should be made. J. W. M.

Micro-determination of Fluorine in Organic Substances. D. M. Hubbard and A. L. Henne. (*J. Amer. Chem. Soc.*, 1934, 56, 1078–1080.)—The method consists in decomposing the organic molecule over silica heated to 900° C. in a combustion tube. The silicon tetrafluoride formed is collected in water or in a weak alkaline solution, and the fluorine ion is titrated by means of cerous nitrate. It is essential to sweep out the combustion tube with hydrogen to remove adsorbed silicon fluoride and to reduce silicon oxyfluoride. Gases containing both fluorine and chlorine were analysed, as the chlorine can be determined in the same sample. *Detail.*—About 10 ml. of the sample are measured accurately in a mercury gas-burette, and the volume is increased to 100 ml. by admitting 90 ml. of air or oxygen. The mixture is then forced slowly through the combustion tube, which consists of a 30-cm. silica tube packed with crushed silica graded to 20–40 mesh, and held in place with glass wool. Moist strips of cloth dipping into water are used to keep the ends cool. The middle portion of the combustion tube is heated by means of an electric furnace consisting of a silica-tube, 17·5 cm. long and 15·5 mm. internal, and 22 mm. external diameter, wound round with 7·2 m. of No. 30 nichrome wire over 15 cm. of its length. The whole is wrapped in insulated packing and a rheostat is used to allow of adjustment of temperature. A second 100 ml. of air or oxygen is forced slowly through the burette, followed by 100 ml. of nitrogen, 200 ml. of hydrogen and finally 100 ml. of nitrogen. By this time the fluorine is all carried into the absorption tube as silicon tetrafluoride, and the chlorine as chlorine. The absorption tube consists of a U-tube, 12 mm. in diameter, constricted several times to make 9 successive bulbs, with a horizontal tube connected with the combustion tube by means of a small piece of rubber tubing. The absorption tube contains 10 ml. of 0·1 per cent. sodium hydroxide solution and 1 ml. of superoxol, to hydrolyse the silicon tetrafluoride and to reduce the chlorine to hydrogen chloride. The chlorine is titrated by the usual Volhard method, and the fluorine is titrated by a modification of Batchelder's method (Batchelder and Meloche, *J. Amer. Chem. Soc.*, 1931, 53, 2131). The contents of the tube are washed with 150 ml. of water into a 250-ml. beaker, 1 ml. of superoxol is added, and the mixture is boiled to remove excess of hydrogen peroxide. The silica is filtered off, and the filtrate is diluted to 250 ml. A 25-ml. portion is neutralised with N nitric acid, and finally with 0·02 N nitric acid, with phenol red as indicator. After each addition of acid the solution is heated to remove carbon dioxide, and, when neutral, it is evaporated to 5 ml. (not more), and 2 drops of methyl red and 10 drops of bromcresol green indicator solution are added. A green colour develops. The mixture is titrated at 80° C., with frequent shaking, against a solution of cerium nitrate hexahydrate (7·6206 grms. in 2 litres; 1 ml. $\equiv$ 5 mgrms. of fluorine), using a micro-burette. The end-point is taken at the maximum strength of purplish-red colour, viewed preferably by transmitted light. Very accurate results were obtained, the differences from the calculated being less than 1 per cent. The accuracy with which the sample can be measured is shown to be the limiting factor in the accuracy of the results. J. W. M.

Micro-method for the Determination of Free and Combined Cholesterol. R. Schoenheimer and W. P. Sperry. (*J. Biol. Chem.*, **1934, 106,** 745–760.)—The method consists in the precipitation of cholesterol with digitonin, followed by the application of a colour reaction to the precipitate, and it is claimed that 0·02 to 0·15 mgrm. of cholesterol may be determined in 0·2 ml. of blood or serum at the rate of sixteen to eighteen analyses per day. Approximately 3 ml. of a mixture of acetone and absolute alcohol (1 : 1) are placed in a 5-ml. volumetric flask and heated to boiling on a steam-bath; 0·2 ml. of serum or blood is added slowly to the hot solution from a capillary pipette with shaking. The stopper is inserted, and the flask is then shaken vigorously to break up any clumps of protein which may have formed. The stopper is removed and washed, and the contents of the flask are again heated to boiling. The flask is cooled to room temperature, and the contents are made up to volume with acetone and alcohol, mixed thoroughly, and filtered through a small dry filter; the filtrate should be clear. For the precipitation of free cholesterol, 2 ml. of the filtrate are pipetted into an ordinary 15-ml. conical centrifuge tube, 1 ml. of digitonin solution is added, and the solution is stirred thoroughly with a stirring rod, which is left in the tube. The tube is placed in a preserving jar (pint or quart size), the cover is placed on tightly, and the jar is left overnight at room temperature. After standing, the tube is removed to a test-tube rack, and the solution is stirred gently to free particles of precipitate which may adhere to the walls of the tube; the stirring rod is removed carefully without touching the upper part of the tube, and laid on a rack so that no adherent precipitate is rubbed off; the tube is then centrifuged at about 2500 r.p.m. for 15 minutes. The supernatant solution is drawn off slowly with a fine capillary pipette to which suction is cautiously applied with a pump. Care is taken not to touch the wall of the centrifuge tube with the pipette or to stir up the precipitate. A few particles, which are probably cholesterol ester, usually float at or near the surface and are drawn off with the solution. The stirring rod is placed in the tube, and the tube and rod are washed with 1·5 to 2·0 ml. of acetone-ether (1 : 2) from a dropping pipette. After stirring, the rod is removed as before, the tube is centrifuged for five minutes, and the supernatant solution is again removed. The precipitate is then washed twice more in this manner with ether alone. After the last washing the rod is placed in the tube, which is dried by immersion in a water-bath at 40° C. The dried precipitate of cholesterol digitonide is now dissolved in 1 ml. of glacial acetic acid, care being taken that all particles adhering to the sides of the tube are dissolved. Warming to 60° C. may hasten this solution. The tube is then placed in a water-bath at 25° C. in the dark and left for a few moments. It is then removed, and 2 ml. of acetic anhydride are added, followed by 0·1 ml. of concentrated sulphuric acid, preferably from an automatic micro-burette. The solution is now stirred vigorously (the rod still in the tube), and the tube is replaced in the water-bath in the dark. At any time between 27 and 37 minutes after addition of the sulphuric acid the colour can be determined, and other tubes may be similarly treated in the meantime. The colour may be determined in a Pulfrich photometer or a colorimeter, using a solution of anhydrous cholesterol in acetic acid as a standard. The total amount of cholesterol may be determined by pipetting 1 ml. of the acetone-alcohol extract, into a centrifuge tube, adding to it one drop of potassium hydroxide solution (10 grm. of pure KOH in 20 ml. of water), and stirring with a stirring rod, which is left in the tube. The tube is then placed in a preserving jar containing a layer of sand about 3 cm. deep, which has been heated to about 40° C. The cover is clamped on tightly, and the jar is kept at 37–40° C. for half an hour. After hydrolysis the tube is cooled, 1 ml. of acetone-alcohol solution is added, and the solution is titrated with 5 per cent. hydrochloric acid, phenolphthalein being used as an indicator. The solution is stirred after the addition of each drop, and care is taken to insure that a definite excess of acid is present; 1 ml. of digitonin solution is added, the solution is stirred thoroughly, the tube centrifuged for 5 minutes, and washed as in the determination of free cholesterol, except that only one washing with ether is necessary. The colour reaction is then carried out as previously described. The ether used in this work was purified by washing with sodium sulphite, then several times with water, and finally distilling over calcium chloride. The digitonin solution was prepared by dissolving 1 grm. of digitonin in 1000 ml. of water, and the solution was kept in ice for at least twenty-four hours. The supernatant solution was filtered and concentrated to 500 ml. by immersing the containing flask (preferably having inlet and outlet tubes) in boiling water, and drawing air through the space above the liquid. The original paper is supplemented by numerous footnotes commenting on the process. S. G. S.

Microchemistry of Atophan. M. Wagenaar. (*Pharm. Weekblad,* 1934, **71**, 1100–1103.)—Atophan (phenyl cinchoninic acid) is insoluble in water, but soluble in alcohol, ether or solutions of alkalis. It is best prepared for the undermentioned tests by sublimation (at approximately 200° C.), but this requires care, as some carbon dioxide may be liberated, and it is not quantitative for amounts of less than 1 mgrm. According to van Zijp (*id.*, 1930, **67**, 192) hydriodic acid containing a little iodine produces brown droplets which deposit brown needles; if a solution of iodine in potassium iodide solution is present, these appear as dark blue or black star-shaped aggregates. Denigès (*Mikrochemie*, 1931–1932, **10**, 430) evaporated a solution of atophan in ammonia, and noted the formation of star-shaped aggregates of negative double-refracting crystals at the edges of the drop; addition of sulphuric acid to this solution gave a heavier precipitate containing numerous globular aggregates. The present author, however, obtained better results with hydrochloric acid or ammonium chloride (sensitiveness 0·05 mgrm., 1 : 200), or with nitric acid or ammonium nitrate (0·1 mgrm.); other ammonium salts also gave good results, but precipitation of solutions of atophan in sodium hydroxide solution with sodium chloride or sodium sulphate was less successful. If a crystal of atophan is suspended in a solution of iodine in potassium iodide solution and a drop of dilute sulphuric, selenic or phosphoric acid is added, a precipitate results which is soluble on addition of acetone; on evaporation the resulting solution deposits red-brown or grey dichroic plates (sensitiveness 0·05 mgrm., 1 : 200). Similar, but less sensitive, results are obtained with organic acids, or by adding an excess of glacial acetic acid and a drop of acetone to a solution of the crystal in ammonia. A mixture of a crystal of atophan, chloral hydrate, the iodine-iodide reagent and a drop of dilute hydrochloric acid deposits matted masses of blue crystals, the colour of which is removed by sodium thiosulphate solution (*cf.* narceine and coumarin) and varies in shade according to the concentration of the acid. A crystalline bromine-addition product is formed, usually as yellow crystals, by suspending a crystal of the sample in bromine water (sensitiveness 0·1 mgrm.). Photo-micrographs of some of the crystals are given.

J. G.

Physical Methods, Apparatus, etc.

The "Brittle-Point" of Bituminous Road Materials. W. E. Golding and F. M. Potter. (*Chem. and Ind.*, **1934**, **53**, 628–629.)—An examination has been made of the Fraass Test (*Asphalt und Teer*, **1930**, **13**, 367, *World Petroleum Congress*, **1933**), which is a method for the determination of the temperature at which plastic binders, *e.g.* asphalt, employed in road construction, pass from the plastic to the brittle state. An apparatus is employed in which a thin steel strip, previously coated on one side with a layer of binder of standard thickness, may be bent while it is kept inside a glass tube supported in a transparent vacuum flask which contains the cooling medium. The authors prefer to use a mixture of carbon dioxide snow and ether as giving the best control of the rate of cooling. The rate of fall of temperature is adjusted to not more than one degree per minute, and the test-strip is bent at each degree fall in temperature, commencing at about 10° above the expected brittle-point. The break is observed by illuminating the strip. The standard quantity of binder for each test is 0·4 ml., and may be weighed on to a steel strip or delivered from a small press. The mould of the press is cylindrical (20 mm. in diameter by 20 mm. high), and in the bottom is a slit 20 mm. long by 0·5 mm. wide, through which is extruded a strip of standard dimensions. The binder is applied to the steel strip (40 mm. by 20 mm. by 0·15 mm.), and the projecting ends removed. The steel strip with the layer of binder is carefully heated on a horizontal steel plate until air and moisture have been removed. The final removal of minute air bubbles from the surface is accomplished by the careful passage of a pinhead gas flame over the surface of the binder. When cool, the test-piece is placed in the clip of the bending apparatus. Results obtained by this process, while probably sufficiently good for ordinary work, were somewhat variable, owing to factors which could not be sufficiently well controlled, *viz.* variations in the thickness of the asphalt layer and slight differences in the individual heating of each strip, which affected the degree of adhesion of the material to the steel. It was found better to weigh out 0·4 ml. of the material on to each steel strip, and to allow the binder to spread itself over the strip by standardised heat treatment. Heating in a hot-air oven at 105° to 110° C. for 20 minutes was satisfactory for a binder of the consistency of standard paving asphalt, but, for a softer material, a lower temperature and a shorter period of heating would probably suffice. With samples of residual bitumen, the break at the brittle-point consisted of a single fracture across the strip, with the broken ends standing away from the bent steel support. Coal-tar products adhered more strongly to the steel, and at the brittle-point the material remained adherent and merely showed cracks.

S. G. C.

Spectroscopic Determination of Fluorine in Water. A. W. Petrey. (*Ind. Eng. Chem., Anal. Ed.*, 1934, 6, 343–345.)—The method is based on the appearance of the calcium fluoride band spectrum (in which the band with head at λ5291 is the most sensitive part) in the spark or arc spectrum of the mineral residue of the water, and it is suitable for waters containing about 0·025 to 1·5 per cent. of fluorine in the residue. About 12·5 mgrms. of residue, obtained by evaporation of the water, observing the usual precautions, and ignited at about 500° C., are tightly pressed into the cavity of a graphite anode which has been impregnated with calcium chloride; a copper cathode is used. The residue is completely volatilised by arcing, the spectrum being photographed meanwhile. The spectrum is compared with standard spectra after optical projection on an aluminium screen. The standards are prepared by adding sodium fluoride solution to a suspension of calcium carbonate, evaporating off the water, and thoroughly pulverising the residue; a range of 7 standards containing 0·025 to 1·5 per cent. of fluorine should be prepared, and the spectra photographed. In testing waters containing a considerable amount of salts, a similar quantity of these should be introduced into the carbonate-fluoride standards. Alternative to the photographic method, a visual method may be used in which the time required for the disappearance of the calcium fluoride spectrum is noted; the amount of fluoride present may be read from a curve obtained by plotting the concentration of fluoride with the time for disappearance of the spectrum in a series of standards prepared as for the photographic method. The visual method is limited to residues consisting essentially of calcium and magnesium salts. S. G. C.

Reviews

THORPE'S DICTIONARY OF APPLIED CHEMISTRY. Supplement Vol. I, A–M. By J. F. THORPE, D.Sc., F.R.S., and M. A. WHITELEY, D.Sc., and eminent contributors. Pp. 680. London: Longmans, Green & Co. 1934. Price 60s.

Seven years have passed since the last volume of "Thorpe" was published—13 years since the first volume of the edition—during which time very great advances have been made in technical chemistry. We are told, and verily believe, that the best method of bringing the Dictionary up to date was the subject of earnest discussion between Editors and Publishers. This volume is part of the result. Two supplementary volumes are being issued dealing with sections in which the greatest advances have been made, and the contributors give concise accounts of the present state of knowledge in their sections. Much new knowledge and many new subjects are also included.

It is impossible adequately to comment on all the matter in the volume before us; suffice to say that it follows the style and maintains the excellent standard to which we have become accustomed in Thorpe's Dictionary. Whatever a chemist's special branch, his bookshelf is not complete without "Thorpe," and now will not be complete without the supplement. One method open to a reviewer of such a volume is to dip into it somewhat as one does into a bran tub; another, perhaps better is to take the volume into use and refer to it on all the problems that arise in the analyst's laboratory in the course of a month or so. The reviewer has applied both methods and is well satisfied with the results. All the articles tested are good; some are excellent.

Perhaps the first section to mention is "Analysis"—30 pages—from the able and versatile pen of Professor Morgan; all the new organic substances recently introduced for the determination of various metals are described in sufficient detail, also new volumetric and gravimetric processes for rare, as well as common, elements and radicles. Carbohydrates occupy about 20 pages, largely indicating the new views on structure, but new sugars and uronic acids are all included. Carbon tetrachloride, decolorising carbons and other subjects receive the detailed treatment concordant with their increased industrial importance. There is a long section on the new dyes, including those for artificial silks and union fabrics. Co-ordination compounds, chemical warfare, corrosion, enzymes, explosion, explosives . . . the list is almost endless, glue, glycerine, iron and steel, hafnium, ketenes, milk. One lingers on milk with some disappointment, as the opportunity has been missed of an authoritative survey of such matters as spray- and roller-dried milk, condensed milk, tinned cream, and of the controversy between the advocates of pasteurisation and non-pasteurisation. A critical outline of recent work on the freezing-point would have been welcomed. It appears that our knowledge of the real constitution of milk has hardly advanced at all.

Perhaps the aspect which most deserves commendation is the skill with which editors and authors have selected their subjects and balanced theoretical matter with industrial practice. The distinction between "pure" and "applied" chemistry is rapidly vanishing, as no new chemical industry can flourish without sure theoretical foundation; the theoretical knowledge of to-day is the industrial practice to-morrow. So our Editors have seen to it that the theory underlying almost every technical product with which they deal is adequately described. The publication of this supplement will further secure for "Thorpe" the unique place it has long held in English chemical literature. It is the first place to turn to on an unknown problem; the details required may not be found, but usually there will be general information and references showing where further knowledge is to be obtained. It is one of the most nearly "indispensable" books we have.

H. E. Cox

GERMAN-ENGLISH CHEMICAL TERMINOLOGY. By A. KING and H. FROMHERZ. Pp. xvii + 324. London: T. Murby. 1934. Price 12s. 6d. bound.

As stated on the folder, "the object of this book is primarily to aid English-speaking and German students, scientists and other people interested in chemistry and its allied subjects, to acquire a knowledge of the chief terms used in the chemical literature of the language foreign to them," and, it might be added, to acquire a knowledge of the language in general and the structure of sentences. The chemical terms are introduced by writing a text-book of chemistry in English and German printed on opposite pages so that each paragraph is directly opposite to its literal translation. When a term is introduced for the first time it is printed in italics, and the book contains over 4000 expressions.

The subject-matter is divided into elementary, inorganic, organic and physical chemistry, with a chapter on modern theories of the structure of matter, and appendices consisting of a table of atomic weights, mathematical expressions, and a useful list of both English and German abbreviations. There is a competent index in both languages.

The range of terms included is extremely large; for example, the section on laboratory equipment and apparatus covers terms used in glass-blowing and soldering as well as names of general apparatus, including equivalents such as "carboy of acid," "Säure ballons," among the less-known terms which can be very useful to a student working in a foreign laboratory.

This method of learning German is vastly superior to ordinary translation with a dictionary, since not only is the correct translation given, but the term is also described in its context. The text has obviously been very carefully written by both authors, so that a literal translation is possible, and the subject-matter is well graduated, so that the later chapters are more difficult both in language and in chemistry.

As a means of studying German the book is to be recommended both to preliminary and advanced students. Those who consider themselves familiar with the German language will be surprised to find the large number of useful expressions that are new to them. The book is also valuable to those who have to compose letters in German to scientific colleagues.

A secondary use of the book is that it is also a very clear concise textbook of chemistry, both for students and for specialists who wish to refer to elementary facts or theories of other branches of chemistry. In this connection such a section as that on crystallography and the description of crystallographic series, which is not available in most textbooks of elementary chemistry, is very useful.

The section on inorganic chemistry (50 pp.) contains a brief description of the non-metallic elements, a sub-section on qualitative analysis consisting of a description of dry tests and group separations, and tests for anions. Since the book is not intended primarily as a textbook, only the conventional methods are described, and these include neither micro methods nor "spot" tests. There is also a well-written chapter on the technical preparation and uses of metals. The organic section (50 pp.) contains a brief description of the main groups of aliphatic and aromatic compounds, and a note on the enzymes. The section on physical chemistry (70 pp.) is the most complete and is the most useful when the book is to be used for reference.

The authors are to be congratulated on having successfully achieved a dual purpose.

JANET W. MATTHEWS

REPORT OF THE SOCIETY OF DYERS AND COLOURISTS ON THE WORK OF THE FASTNESS COMMITTEE IN FIXING STANDARDS FOR LIGHT, PERSPIRATION AND WASHING. ANON. Pp. 52. Bradford: The Society of Dyers and Colourists. 1934.

This little book will be read with considerable interest by all concerned with textiles or dyes, whether from the technical or analytical point of view. This statement applies, perhaps, most forcibly to the section dealing with fastness to light, as will be appreciated by those who have become accustomed to seeing their laboratory windows decked out with coloured strips undergoing fading-tests, or who have many times waited in vain for the sun to shine.

It is now recognised that the carbon arc is the most suitable source of light for accelerated laboratory fading tests, and two types of these lamps are described, in which provision is made for exposure under controlled conditions of temperature and humidity. In the case of daylight tests, samples are graded into 8 categories by exposing them simultaneously and under specified conditions with 7 red and 7 blue standardised dyeings on a specified worsted serge; the dyes were selected so as to form a series showing a regular gradation in the degree of fastness, independent of temperature, humidity, atmospheric impurities and the quality of the light source. If one may venture on criticisms of such a method, they are first, that a set of standards must be sacrificed for each test, with the consequent possibility of "wandering" from the original shade when successive batches are made up over a long period of time; and, secondly, that the degree of fastness of the sample, unlike that of the standard, may not be independent of the quality of the light. There is something, therefore, to be said for a method in which the time of exposure is determined by the total amount of active light falling alike on the standard and sample (*cf.* ANALYST, **1934**, **59**, 439), even if such a method is open to other objections.

The work on perspiration tests involved determinations of the compositions and properties of perspiration itself, and is of great interest and importance on this account alone. On the basis of this work, formulae for synthetic acid and alkaline perspiration liquors have been evolved, corresponding with freshly-shed and old excretions, respectively. The reviewer has found (from experiments in connection with the handling of acid- and alkali-sensitive security-papers) that the sweat of Asiatics has a lower p_H value than that of the average Englishman in the marketing of textiles for export; this difference may well give rise to a problem for which the present Report provides little assistance. However, the test described (which involves incubation at 37° C. for 4 hours) should always give an indication when a particular dye is totally unsuitable for human wear.

Four washing-tests are suggested, which vary in severity from the equivalent of a mild home-wash to the effect of four of the more devastating laundry-washes. A wheel-type washing machine of standardised design is described, and a series of ten red and blue standard dyeings enables the results to be classified by comparison.

The bridging of the gap between empirical and exact science is never an easy one. The Society is, therefore, to be warmly congratulated on the success with which it has achieved its particularly difficult task, since there is not the least doubt that the methods described will bear favourable comparison with those suggested by similar bodies in other countries.

JULIUS GRANT

DECEMBER, 1934

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Vol. 59, No. 705

THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

An Ordinary Meeting of the Society was held at the Chemical Society's Rooms, Burlington House, on Wednesday, November 7th, the President, Mr. John Evans, being in the chair.

Certificates were read in favour of:—Arthur James Amos, Ph.D., B.Sc., A.I.C., Harry Ronald Fleck, A.I.C., Walter Lee, A.I.C., Edward Burdon Parkes, M.Sc., A.I.C., Francis Cecil Storrs, B.Sc., A.I.C., James Thompson, Ph.D., F.I.C., Robert Sinclair Watson, A.I.C.

The following were elected Members of the Society:—As Honorary Members: Gilbert Thomas Morgan, O.B.E., D.Sc., LL.D., A.R.C.S., F.R.S., Jocelyn Field Thorpe, C.B.E., Ph.D., D.Sc., F.R.S. As Ordinary Members: Victor Cecil Branson, A.R.C.S., D.I.C., B.Sc., A.I.C., Roydon George Cowdell, Joseph Davies, F.I.C., Frank Akerman Hatch, A.I.C., Herbert Lloyd Hind, B.Sc., F.I.C., Alexander Marr, A.M.C.T., Daniel Donald Moir, M.Sc., F.I.C., Teunis Potjewijd, D.Sc., Magnus A. Pike, B.Sc., Walter James Rees, M.Sc., F.I.C., James Sandilands, F.I.C., William Wilders Taylor, B.Sc., F.I.C., William Pearson Thistlethwaite, B.Sc., Frederick Thomas, M.Sc., Dennis Gordon Tompkins, B.Sc., A.I.C.

A discussion was held on

Quantitative Spectroscopy and its Analytical Applications.

The discussion was opened by Dr. J. J. Fox, who was followed by Mr. F. Twyman (speaking on Apparatus), Dr. S. Judd Lewis (on Methods of Spectroscopy), and Mr. D. M. Smith (on the Application of Spectroscopic Methods to Metals).

JOINT MEETING WITH THE FOOD GROUP OF THE SOCIETY OF CHEMICAL INDUSTRY

A Joint Meeting of the Food Group of the Society of Chemical Industry with the Society of Public Analysts was held at the Chemical Society's Rooms, Burlington House, on Wednesday, November 14th, Dr. L. H. Lampitt, F.I.C., Chairman of the Food Group, being in the chair.

The following papers were read and discussed:—"The Identification of Common Edible Sea Fish" (with demonstration), by C. H. Hattersley (Chief Inspector, Fishmongers' Company); "Fish Oils and their Vitamins," by Norman Evers, B.Sc., F.I.C.; "The Composition of Fish Pastes," by H. E. Cox, D.Sc., F.I.C.; "Note on Fish Pastes," by C. H. Manley, M.A., F.I.C.; "Some Observations on the Amounts of Amines and Free Ammonia in Fish Products," by D. H. F. Clayson, B.Sc., F.I.C., and L. H. Lampitt, D.Sc., F.I.C.; and "Some Observations on Methods of Estimating the Degree of Preservation of White Fish," by G. A. Reay, Ph.D. (Torry Research Station).

REPORTS OF THE SUB-COMMITTEES OF THE STANDING COMMITTEE ON THE UNIFORMITY OF ANALYTICAL METHODS*

THE Council have specifically endorsed the recommendations of the Standing Committee and have adopted all the Reports which have hitherto been published. The following is a list of the Reports endorsed by the Council:

Milk Products Sub-Committee:

Milk Products.	Report No. 1. Report No. 2.
Report No. 3.	Analysis of Sweetened Condensed Milk in which the Sucrose has altered during Storage.

Essential Oil Sub-Committee:

Report No. 1.	Estimation of Cineole in Essential Oils. (1) Cajuput and Eucalyptus Oils.
Report No. 2.	Physical Constants (1).
Report No. 3.	Physical Constants (2).
Report No. 4.	Interim Report on the Determination of Acetylisable Constituents in Essential Oils.
Report No. 5.	Determination of Phenols in Essential Oils.
Report No. 6.	Determination of Citral in Lemon Oil.
Report No. 7.	Determination of Solubilities.
Report No. 8.	Determination of Cineole in Essential Oils. (2) Camphor Oil. (3) Other Oils.
Report No. 9.	Determination of Carvone and Menthone.
Report No. 10.	Determination of Citronellal.
Report No. 11.	Determination of Aldehydes other than Citronellal.

Sub-Committee on the Determination of Arsenic, Lead, etc.:—

Report No. 1.	Determination of Arsenic.

Sub-Committee on the Determination of Unsaponifiable Matter in Oil and Fats and of Unsaponified Fat in Soaps:

Report No. 1.	Determination of Unsaponifiable Matter in Oils and Fats.

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* The Reports are obtainable only from the Editor of THE ANALYST, 85, Eccleston Square, London, S.W.1, on prepayment of the advertised prices.

The Determination of Traces of Lead in Biological Materials, with Special Reference to Bone

By G. ROCHE LYNCH, O.B.E., M.B., B.S., D.P.H., F.I.C.
R. H. SLATER, D.Sc., Ph.D., F.R.S.E., A.I.C., and
T. G. OSLER, M.B., Ch.B., M.R.C.S., L.R.C.P.

(*Read at the Meeting, October* 3, 1934)

Introduction.—The great importance of the detection and determination of lead in the human body, and in biological and industrial materials generally, has been realised for a considerable time; the interest taken in investigations of this nature is shown by the voluminous literature and frequent articles published on the subject (*cf.* Analyst, 1932, 57, 775). It has been definitely established from chemical investigation of experimentally lead-poisoned animals, and from clinical cases of plumbism, that when lead is taken into the organism and absorbed, that part which is not excreted by the kidneys, liver and intestine, and which in chronic plumbism represents nearly all the absorbed lead, is taken up from the circulating blood by the bones under normal conditions and held there in a comparatively innocuous and permanent form. In spite of this knowledge, very little work appears to have been done on the lead-content of "normal" bones.

The difficulty of devising a satisfactory method for the determination of lead in biological materials, especially bone, has been emphasised by numerous authors in the past. The methods previously described (with one or two notable exceptions) involve ashing at some stage or other, often for prolonged periods at dangerously high temperatures, which involve the possibility of loss of lead by volatilisation; this constitutes a very serious criticism of these methods and their results. In undertaking this work it was therefore essential to devise an accurate, and, if possible, simple process which would avoid or overcome the defects present in previous methods, and so establish the limits of lead present in normal bones with more certainty and accuracy than are afforded by former methods. These "normal" figures having been established, it would then be possible to draw comparisons with the results of analyses of bones from cases of frank or suspected plumbism; this, in our opinion, constitutes a question of considerable clinical and toxicological importance.

Discussion of Method of Analysis

Bone.—We have used wet oxidation with nitric and sulphuric acids, and in our hands this has proved very satisfactory, 4 grms. of bone taking 4 to 7 hours for oxidation, which is a shorter time than that usually required for complete ashing. We stress the importance of wet oxidation as opposed to ashing, for it must be emphasised that destruction at a temperature above 550° C. will result in loss of lead, and it is possible that prolonged heating at even lower temperatures may result in some loss. Where very small amounts of lead are involved this becomes a possible source of serious error.

After resolution of the bone to its inorganic constituents in sulphuric acid, the next stage was the determination of the lead. It was thought that extraction of the lead by means of diphenylthiocarbazone (Allport and Skrimshire, ANALYST, 1932, 57, 440) might prove to be simple and satisfactory, and would thus avoid the more complicated electrolytic deposition methods. The use of diphenylthiocarbazone for extraction of lead has been described by the abovementioned workers, who employed it in the determination of traces of lead in dyestuffs, and suggested its use for other organic materials. Lead can be extracted quantitatively by this reagent only from its alkaline solution, which must be absolutely clear and free from adsorbing substances. When a large amount of lead is present a smaller initial quantity of the material than would usually be employed should be taken, on account of the insolubility of certain lead salts under these conditions, and the method and quantities of reagents modified accordingly. We have not determined the maximum amount of lead that can be extracted under the conditions of our experiments, and on this account have avoided, wherever possible, working with quantities of material containing more than 1·0 mgrm. of lead. We have found that 0·25 to 0·50 mgrm. of lead is a convenient amount to extract and determine.

It is obvious that the diphenylthiocarbazone process of extraction cannot be applied at once to the products of wet oxidation of bone, since large amounts of calcium and phosphate ions are present in the mixture, which would result in a bulky precipitate of calcium phosphate separating out on alkalisation. Calcium phosphate can be held in solution in alkaline medium by means of ammonium citrate, but its use here is impracticable on account of the large quantity of citrate which would be necessary to ensure complete solution of the great amount of calcium phosphate present in the bone, and the consequent large volumes which would have to be extracted.* In order to obtain the conditions required for this extraction, using small volumes, we have separated the calcium component of the bone from the phosphorus component by appropriate chemical manipulations, as suggested to us in a private communication from Dr. Dyer. Each component can then be readily held in alkaline solution in a convenient volume under the necessary conditions, and the lead extracted by diphenylthiocarbazone (0·1 per cent. w/v in chloroform). This reagent extracts only lead and bismuth under these conditions; should bismuth be present, it must be subsequently dealt with, as it forms a black sulphide which would interfere with the colorimetric determination of the lead.

The bismuth-content of bone (and other tissues) has been assumed by several investigators to be negligible, except where medication by bismuth has been practised, especially by parenteral administration. Its possible presence, however, must be borne in mind in any method which extracts bismuth as well as lead (such as the diphenylthiocarbazone process), and in which the lead is determined colorimetrically as the sulphide. In order to detect the presence or absence of bismuth we have used the potassium chromate and the pyridine thiocyanate methods (Hamence, ANALYST, 1933, 58, 461), either of which may be conveniently applied to the residues, with suitable modifications, after determination of the lead or the bismuth, or both. No bismuth has been found in our experiments, and therefore the necessity for removing it did not occur; but, had bismuth been present, we should have been compelled to separate it from the lead. This can be done by electrolysis of a solution of the mixed nitrates or by the pyridine thiocyanate method of separation.

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* Subsequently to the commencement of this work an article appeared on the determination of lead in acid calcium phosphate by Kent-Jones and Herd (ANALYST, 1933, 58, 152), which applies the method of lead extraction of Allport and Skrimshire from the calcium phosphate directly, the latter being held in alkaline solution by ammonium citrate.

The method for the determination of lead in marrow is the same as for bone. Wet oxidation takes a longer time on account of the large proportion of fat present.

FOR OTHER BIOLOGICAL MATERIALS.—Having found the method to be satisfactory for bone, we applied it to other biological materials, *e.g.* urine, faeces, blood and organs.

The process for bone and other biological materials takes 1 to 2 days to complete, this depending upon the type and the amount of tissue to be analysed, and by this method 0·02 mgrm. of lead can be accurately determined.

DESCRIPTION OF THE METHOD

PRELIMINARY NOTE.—As the amounts of lead present in biological materials are very small, it is essential to prevent, as far as possible, adventitious gain of traces of lead and to know accurately the amount so picked up during the course of an experiment. Distillation, or careful selection, or both, will enable samples of the reagents required to be obtained, either free from lead or containing such small amounts of the metal that these may be neglected or compensated by small equivalent subtractions, and checked by blank experiments. Periodical blank determinations should also be made for lead in order to ascertain if any lead is being taken up from the apparatus or any other source. Precautions must be taken against lead contamination of the distilled water.

The process has been tested rigorously by blank and control experiments as follows:

Since it appears impossible to obtain lead-free bone, blank experiments have been carried out, using as the initial material a practically lead-free sample of potassium carbonate (4 grms.). In addition, controls on bones and other tissues have been undertaken by taking two or more portions and adding a known amount of lead in some experiments prior to the commencement of wet oxidation. In every case it was found that the added lead was satisfactorily recovered. The residues obtained from solutions A and B (see Fig. 1) in one bone experiment after extraction of the lead by the diphenylthiocarbazone reagent were ashed at a bright red heat for many hours, and then re-extracted after addition of known amounts of lead to different fractions. Here, again, it was found that the added lead was satisfactorily recovered.

The results of the control experiments on bone and other organic materials appear in the respective Tables and those from the other control experiments and the "blanks" are given in Table I. These results demonstrate that, under the conditions of our experiments, the lead is completely extracted.

TABLE I

BLANKS AND CONTROLS

Twenty grms. of a sample of potassium carbonate were found to contain 0·01 mgrm. of lead by direct colorimetric estimation; hence 4 grms. contain 0·002 mgrm. of lead.

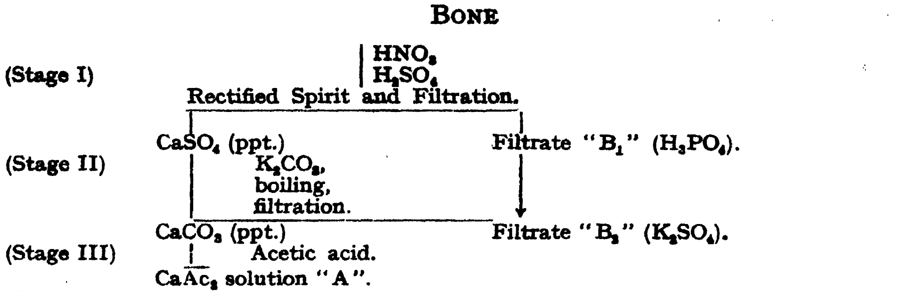
Experiment.	Lead added Mgrm.	Lead found Mgrm.	
Blank, 4 grms. of K_2CO_3, 6 expts. performed	Nil	0·025 to 0·05 (derived from other chemicals used)	
Control, 4 grms. of K_2CO_3	0·02	0·024	(These figures were obtained after allowance had been made for the lead picked up from the other chemicals, a blank having been performed in each case)
,,	0·02	0·025	
,,	0·05	0·045	
,,	0·20	0·19	
,,	0·50	0·50	
,,	1·00	1·05	
Control, bone solution A	0·05	0·055	(Ditto)
,, ,, A	0·50	0·475	
,, ,, B	0·05	0·05	
,, ,, B	0·20	0·21	

A = $Ca^{\cdot\cdot}$ fraction (v. Fig. 1)
B = PO_4''' fraction (v. Fig. 1)

REAGENTS

1.	Nitric acid, A.R.	100 ml. found to contain 0·02 mgrm. of lead
2.	Sulphuric acid, A.R.	10 ,, ,, ,, ,, 0·02 ,, ,,
3.	Rectified spirit, redistilled	100 ,, ,, ,, ,, Nil
4.	Acid-alcohol mixture (H_2SO_4 1 per cent. in redist. rect. spirit 80 per cent.) ..	100 ,, ,, ,, ,, Nil
5.	Potassium carbonate, A.R.	20 grms. ,, ,, ,, 0·01 mgrm. ,,
6.	Glacial acetic acid, A.R., redistilled..	20 ml. ,, ,, ,, Nil
7.	Ammonium hydroxide, A.R. (*d* 0·880) ..	100 ,, ,, ,, ,, 0·01 mgrm. ,,
8.	Ammonium acetate reagent (5 ml. = 2 grms. $H\overline{Ac}$). Prepared from the above reagents	30 ,, ,, ,, ,, Nil
9.	Ammonium citrate reagent (5 ml. = 2 grms. citric acid). Prepared from the above ammonia and citric acid, A.R.	20 ,, ,, ,, ,, 0·02 mgrm. ,,
10.	Sodium cyanide solution (5 per cent. w/v)..	2 ,, ,, ,, ,, Nil
11.	Diphenylthiocarbazone, 0·1 per cent. w/v in chloroform	100 ,, ,, ,, ,, 0·02 mgrm. ,,
12.	Chloroform, A.R., redistilled	200 ,, ,, ,, ,, Nil
13.	Potassium sulphate	2·5 mgrms. ,, ,, 0·01 mgrm. ,,
14.	Copper sulphate solution (1 ml. = 1 mgrm. Cu)	10 ml. ,, ,, ,, Nil

THE METHOD.—BONES, MARROW, TEETH (see Fig. 1). *Stage I.*—The material (2 to 4 grms.) is dissolved in concentrated nitric acid (5 ml.) in a 200-ml. long-necked silica flask by gentle heating. The flask is then cooled, concentrated sulphuric acid (5 ml.) is added, and the flask carefully heated until oxidation commences, after which it proceeds vigorously. When all the nitric acid has been used up in this process, as shown by charring and by the disappearance of brown


BONE
(Stage I)
HNO_3
H_2SO_4
Rectified Spirit and Filtration.
(Stage II)
$CaSO_4$ (ppt.)
K_2CO_3, boiling, filtration.
Filtrate "B_1" (H_3PO_4).
(Stage III)
$CaCO_3$ (ppt.)
Acetic acid.
Filtrate "B_2" (K_2SO_4).
$CaAc_2$ solution "A".

(Stage IV) Solution "A" extracted with diphenylthiocarbazone under the required conditions. Solutions "B_1" and "B_2" combined and extracted similarly. Extracts oxidised.

(Stage V) Lead determined colorimetrically as sulphide.

(Stage VI) Residues examined for bismuth.

FIG. 1.

nitrous fumes, which are replaced by white sulphur trioxide fumes, the flask is allowed to cool, concentrated nitric acid (1 to 2 ml.) is added, and careful heating recommenced. When oxidation is complete, all remaining nitric acid is driven off by boiling with water until fumes of sulphuric acid appear. The contents of the flask, consisting of a white precipitate of calcium sulphate and a supernatant fluid containing phosphoric and sulphuric acids, are transferred to a 250-ml. beaker, and the flask is washed out with water and dilute ammonium acetate solution made faintly alkaline with ammonia. (The total volume in the beaker at this stage should be about 50 ml.) Rectified spirit (about 25 ml.) is now added, and the mixture is allowed to stand in the refrigerator overnight; this permits of the almost complete precipitation of the calcium sulphate.

Stage II.—The calcium sulphate precipitate (see Fig. 1) is filtered off on a small Hirsch funnel and washed with a minimum volume of the acid-alcohol mixture (about 50 ml.), and the filtrate (B_1) is then evaporated down to about 50 ml. The precipitate is washed back with distilled water into the same beaker, using about 50 ml., heated to boiling, and potassium carbonate (4 grms.) in solution in boiling water (50 ml.) added. After being boiled, this mixture is placed on the boiling water-bath for 2 to 4 hours, when the conversion of calcium sulphate into calcium carbonate is complete and the volume has been reduced to 25 to 50 ml.

Stage III.—On cooling, the calcium carbonate is filtered off on the same Hirsch funnel and washed with a minimum volume of potassium carbonate solution (0·5 per cent.). The filtrate (B_2) is added to B_1, which is again evaporated to approximately 50 ml. The calcium carbonate precipitate is washed back into the original beaker with distilled water (about 50 ml.), and sufficient glacial acetic acid is added to effect solution (A). All carbon dioxide is driven off by boiling.

Stage IV.—The two clear solutions, A, containing the calcium component and most of the lead (80 per cent. or more), and B, the phosphorus component, are extracted separately by the diphenylthiocarbazone reagent under the required conditions, *viz.* in alkaline solution, and in the presence of ammonium citrate, ammonium acetate and sodium cyanide. To obtain these conditions, ammonium acetate solution (5 ml.) and a noted volume of ammonium citrate solution (5 to 10 ml.) are added to A and B, which are then made alkaline with ammonia. Sodium cyanide solution (2 ml. of 5 per cent.) is then added to A and B, and each solution transferred to a 150-ml. separating funnel, the volume being made up to about 100 ml. with water and the extraction proceeded with immediately. Precautions must be taken to ensure that the reaction of the mixture remains definitely alkaline throughout the whole of the extraction. Three extractions are made with the dye solution (using 10, 7·5 and 5 ml.), shaking for 2 to 3 minutes, after which 2 to 4 (or more) extractions are made with chloroform only (using 15, 10, 5 ml., etc.), until the last traces of the dye are completely removed from the aqueous mixture. Each extract is washed with water in another separating funnel, and run off into a Pyrex tube (8 × 1 in.) containing a small crystal of potassium sulphate. The chloroform is distilled off and collected for future use. (N.B.—The extracts from A and B may be collected in the same Pyrex tube.) The residue in the Pyrex tube is oxidised by heating with concentrated nitric acid (1 ml.) in the boiling water-bath for 30 minutes, after which concentrated sulphuric acid (0·5 ml.) is added and the tube is heated over a low flame, more nitric acid being added as required. In the presence of potassium sulphate oxidation proceeds rapidly. Copper sulphate (0·5 mgrm.) may be added as a catalyst with advantage, although we have avoided its use when the residue is to be tested for bismuth. When oxidation is complete all remaining nitric acid is boiled off and, after cooling, water (about 20 ml.) is added.

Stage V.—The lead in the residue is determined colorimetrically as sulphide by comparison with a standard solution of lead acetate (1 ml. ≡ 0·01 mgrm. of Pb), according to the method described by Francis, Harvey and Buchan (ANALYST, 1929, **54**, 725). We have found it convenient to prepare the unknown lead solution as follows:

The contents of the Pyrex tube are made alkaline with ammonia, and ammonium acetate reagent (5 ml.) and sodium cyanide solution (2 ml. of 5 per cent.) are added, when a clear colourless solution results. If the amount of lead is known to be small, *e.g.* up to 0·06 mgrm., the whole of this solution is transferred to the Nessler cylinder, and the comparison made directly with the standard lead solution, which is run in from a burette. When the amount of lead is unknown, or known to be large, the solution is made up to a definite volume, *e.g.* 50 ml., and aliquot portions are taken, the necessary adjustments of reagents being made, where necessary, in the Nessler cylinders before adding any sodium sulphide solution. The reason for this is that the most accurate comparisons can be made with 0·04 to 0·06 mgrm. Pb ≡ 4 to 6 ml. of the standard lead acetate solution, when we have found it possible to read correctly to 0·5 ml. (*i.e.* 0·005 mgrm. of Pb).

Stage VI (*Detection of Bismuth*).—(*a*) When the chromate method is to be used for the detection of bismuth, the residues remaining after the lead or bismuth, or both, have been determined are combined, lead and bismuth (if present) are precipitated as their sulphides by hydrogen sulphide under proper conditions, and dissolved in nitric acid. From this a solution in dilute acetic acid is eventually obtained, and chromate added, when lead and bismuth (if present) are precipitated as their insoluble chromates. Sodium hydroxide solution (10 per cent.) is then added drop by drop. The sodium hydroxide converts these insoluble metallic chromates into their hydroxides. The lead hydroxide, being soluble in excess of the alkali, rapidly dissolves, and any bismuth present remains in suspension; we have found it possible by this means to detect 0·05 to 0·02 mgrm. of bismuth in the presence of large amounts of lead (1·0 to 0·2 mgrm.) in control experiments.

(*b*) When the pyridine thiocyanate method, as described by Hamence (*vide supra*), is to be used, the oxidation of the diphenylthiocarbazone residue must be carried out in the absence of copper, and, furthermore, ammonium acetate and sodium cyanide must not be added before the bismuth has been extracted. The reason for this is that we have found that these substances interfere with the extraction of the bismuth. When the diphenylthiocarbazone residue has been completely oxidised, the determination of the lead is carried out as follows: Ammonia is added until alkaline and excess is boiled off, after which concentrated nitric acid (0·5 to 1 ml.) is added, and the Pyrex tube heated, if necessary, to effect solution of all the lead, if this has separated (as it sometimes does, especially when a considerable amount is present). This solution is made up to a definite volume, which is such that 5 to 10 ml. contain a suitable quantity of lead for determination (*viz.* 0·04 to 0·07 mgrm. of Pb). The lead is then determined by placing an aliquot portion in the Nessler cylinder, rendering alkaline with ammonia, adding ammonium acetate reagent (5 ml.), 5 per cent. sodium cyanide solution (2 ml.) and sodium sulphide and comparing with the standard lead solution from the burette. A suitable reading having been obtained, an equal volume is placed in a separating funnel and subjected to the pyridine thiocyanate process for removal of bismuth under the required conditions. In our work we have adjusted the hydrogen-ion concentration of the solution to p_H 5·0 to 5·5 prior to extraction with amyl alcohol and ether. After the extraction the aqueous fraction is filtered into the Nessler cylinder, the filter being washed twice with hot water. This fraction is then made alkaline with ammonia, and the lead is determined in the usual manner after addition of ammonium acetate and sodium cyanide, etc. We have found that the presence of a small amount of ammonium nitrate does not interfere with the determination of lead, and that the method is efficient and satisfactory, *viz.* that traces of lead are not removed, and that small amounts of added bismuth are extracted. If a mixture of bismuth and lead is present, the amount of bismuth can be determined only approximately by this method, for 0·05 mgrm. of bismuth produces with sulphide a colour slightly deeper than that given by the same amount of lead.

FOR ORGANS, BLOOD, URINE, FAECES.—(*a*) *Organs*.—The tissue (10 to 20 grms.) is dissolved in concentrated nitric acid (5 to 10 ml.) by gentle heating. After cooling, a noted volume of concentrated sulphuric acid (5 to 7·5 ml.) is added, and oxidation proceeded with as in the case of bones. The lead is subsequently extracted from the oxidation mixture after dilution with water (50 ml.), addition of ammonium citrate and acetate, ammonia and sodium cyanide (as for bone), and transference to a separating funnel.

(*b*) *Blood.*—Blood (50 to 100 ml.) is evaporated down in a beaker on the boiling water-bath, or boiled down with concentrated nitric acid (10 to 20 ml.) in a silica flask. In the former case the residue is transferred to the silica flask, the beaker being washed out with concentrated nitric acid (10 to 20 ml.), and the flask gently boiled to effect solution. After cooling, a noted volume of concentrated sulphuric acid (5 to 7 ml.) is added, and oxidation commenced by gentle heating. When this is complete, all nitric acid is boiled off and extraction proceeded with in the usual way.

(*c*) *Urine.*—Urine (500 ml.) is evaporated down to about 25 ml., and transferred to a silica flask, all the residue being washed from the evaporating dish with concentrated nitric acid (10 to 20 ml.). Subsequently the process is the same as for blood and organs. (*Note.*—On account of the small amounts of calcium phosphate usually present in the portions of organs, blood and urine taken for analysis, it is not necessary to separate the calcium ion from the phosphate ion prior to extraction of the lead by the diphenylthiocarbazone. It is sufficient to ensure that the calcium phosphate is retained in alkaline solution by the addition of a little ammonium citrate.)

(*d*) *Faeces.*—The dried material (2 to 4 grms.) is dissolved in nitric acid (5 to 10 ml.) in a silica flask by gentle heating. After cooling, a noted volume of concentrated sulphuric acid (5 to 7·5 ml.) is added and the method proceeded with as for organs. If only a small amount of calcium phosphate was present, extraction can be carried out at once (as in the case of organs), but, if not, the calcium and phosphorus components must be separated, as described for bone, prior to extraction of the lead.

The following results were obtained:

TABLE II†

BONE, MARROW, TEETH

Exp.	Weight of fresh bone analysed Grms.	Lead found, as Pb Mgrms.	Lead in fresh bone p.p.m.	Average p.p.m.	Ash from bone Per Cent.	Lead in ashed bone‡ p.p.m.	Case No.	Clinical details
1	S.F. 2	0·22	110	105			1	Unknown.
3	S.F. 2	0·22	100					
4	S.F. 4	0·32	80	80	60	133·5	2	Unknown.
16	S.F. 4	0·34	82·5					
17	S.F. 4	0·31	77·5					
5	S.F. 4	0·155	39	39·5	61·9	64	3	Female. aet. 26. Housewife. Haemorrhage after child-birth.
6	S.F. 4	0·16	40					
9	S.F. 4	0·07	18	14·5	56·8	25·5		Male. aet. 26. No occupation. Pneumonia following head injury.
10	S.F. 4	0·045	11					

TABLE II—*continued.*

Exp.	Weight of fresh bone analysed Grms.	Lead found, as Pb Mgrm.	Lead in fresh bone p.p.m.	Average p.p.m.	Ash from bone Per Cent.	Lead in ashed bone‡ p.p.m.	Case No.	Clinical details
11	S.F. 4	Expt. abandoned		146	63·1	232	5	Male. aet. 53. Railway porter. Brought in dead. Ruptured aneurysm.
12	S.F. 2	0·29	145					
13*	S.F. 4 +0·1 mgrm. Pb. added	0·685 −0·100 =0·585	146					
18	S.F. 4	0·575	144					
26	S.F. 4	0·60	150					
61	UE.F. 4	0·48	120	108	33·2	324		
62	UE.F. 4	0·38	95					
64	LE.F. 4	0·53	133	144·5	32	451·5		
65	LE.F. 4	0·625	156					
19	S.F. 2	0·22	110	120	62·1	193		Male. aet. 72. Occupation unknown. Brought in dead. Heart failure.
20	S.F. 4	0·485	121					
21*	S.F. 4 +0·2 mgrm. Pb. added	0·72 −0·20 =0·52	130					
27	S.F. 4	0·245	61	60·5	60·8	100	7	Male. aet. 46. Waiter. Cancer of throat.
28	S.F. 4	0·24	60					
29*	S.F. 4 +0·2 mgrm. Pb. added	0·40 −0·20 =0·20	50	53	62·4	85		Male. aet. 71. Occupation unknown. Pneumonia following operation.
30	S.F. 4	0·22	55					
31	S.F. 4	0·22	55					
32	S.F. 4	0·065	16	18	62·9	28·5	9	Female. aet. 45. Housewife. Goitre.
33	S.F. 4	0·08	20					
34	S.F. 4	0·25	62·5	64	63·7	100·5	10	Male. aet. 52. Gas company inspector. Cancer of bowel.
35	S.F. 4	0·265	66					
36	S.F. 4	0·14	35	42·5	64·5	65·5	11	Female. aet. 54. Housewife. Heart failure.
37	S.F. 4	0·20	50					
38	S.F. 4	0·205	51	55·5	61·6	90	12	Male. aet. 55. Schoolmaster. Stroke.
39	S.F. 4	0·24	60					
41	S.F. 4	0·14	35	36	60·8	59·5	13	Male. aet. 50. Occupation unknown. Cancer of lung.
42	S.F. 4	0·15	37·5					
43	UE.F. 2	0·067	34	32	45·5	71		
44	UE.F. 4	0·12	30					
45	LE.F. 2	0·08	40	40	50	80		
46	LE.F. 4	0·16	40					

TABLE II—*continued.*

Exp.	Weight of fresh bone analysed Grms.	Lead found, as Pb Mgrm.	Lead in fresh bone p.p.m.	Average p.p.m.	Ash from bone Per Cent.	Lead in ashed bone‡ p.p.m.	Case No.	Clinical details
47	S.F. 4	0·43	107·5	107·5	62	172	14	Male. aet. 55. Night-watchman. Gas-poisoning.
48	S.F. 4	Expt. abandoned						
49	UE.F. 4	Expt. abandoned		45	47	96		
50	UE.F. 4	0·18	45					
51	LE.F. 4	0·43	107·5	114	41	275·5		
52	LE.F. 4	0·48	120					
53	S.F. 4	0·205	51	50	63·9	78	15	Male. aet. 50. Clerk. Lymphosarcoma.
54	S.F. 4	0·195	49					
57	UE.F. 4	Expt. abandoned		20	36·3	55		
58	UE.F. 4	0·08	20					
55	LE.F. 4	0·23	57·5	54	40·4	136·5		
56	LE.F. 4	0·205	51					
80	S.F. 4	0·47	117·5	112·5	62	197·5	16	Male. aet. 57. Cook. Pneumonia.
81	S.F. 4	0·43	107·5					
87	UE.F. 4	0·22	55	53	25·3	209·5		
88	UE.F. 4	0·205	51					
83	LE.F. 4	0·23	57·5	62·5	24·6	250		
84	LE.F. 4	0·27	67·5					
77	M.F. 4	0·10	25	23	—	—		
78	M.F. 4	0·08	20					
79	M.F. 4	0·085	21					
102	S.F. 4	0·12	30	29	54·5	53	17	Male. aet. 3½. No occupation. Acute pneumonic tuberculosis.
103	S.F. 4	0·11	27·5					
110	UE.F. 4	0·11	27·5	26	20·5	127		
111	UE.F. 4	0·10	25					
106	LE.F. 4	0·27	67·5	65	20	325		
107	LE.F. 4	0·25	62·5					
104	M. 4	0·21	50	50	—	—		
119	S.H. 4	0·16	40	41	59	69·5		Male. aet. 72. Occupation unknown. Intestinal obstruction.
126*	S.H. 4 +0·3 mgrm. Pb. added	0·47 −0·30 } =0·17	42·5					
121	S.F. 4	0·20	50	50	58·9	85	18	
122*	S.F. 4 +0·25 mgrm. Pb. added	0·44 −0·25 } =0·19	47·5					
127*	S.F. 4 +0·30 mgrm. Pb. added	0·51 −0·30 } =0·21	52·5					
124	UE.F. 4	0·20	50		27	185		
123	LE.F. 4	0·24	60		27·1	221·5		
125	M.F. 4	0·07	17·5		—	—		

TABLE II—*continued.*

Exp.	Weight of fresh bone analysed Grms.	Lead found, as Pb Mgrm.	Lead in fresh bone p.p.m.	Average p.p.m.	Ash from bone Per Cent.	Lead in ashed bone‡ p.p.m.	Case No.	Clinical details
136	S.H. 4	0·22	55		60·4	91	19	Male. aet. 65. Occupation unknown. Broncho-pneumonia.
129	S.F. 4	0·21	52·5	50	60·3	83		
131*	S.F. 4 +0·25 mgrm. Pb. added	$\left.\begin{matrix}0{\cdot}44\\-0{\cdot}25\end{matrix}\right\}=0{\cdot}19$	47·5					
133	M.F. 4	0·095	24	24				
137	S.H. 4	Expt. abandoned		41	59·9	67	20	Female. aet. 38. Housewife. Heart failure.
139	S.H. 4	0·15	37·5					
150	S.H. 4	0·17	42·5					
140	S.F. 4	0·175	44	44	59·5	73		
153	S.F. 4	0·175	44					
142	UE.F. 4	0·12	30	30	30	100		
143	UE.F. 4	Expt. abandoned						
146	LE.F. 4	0·13	32·5	32·5	26·3	123·5		
147*	LE.F. 4 +0·10 mgrm. Pb. added	$\left.\begin{matrix}0{\cdot}23\\-0{\cdot}10\end{matrix}\right\}=0{\cdot}13$	32·5					
152	F.M. 4	0·08	20	20	—	—		
158	Teeth 4	0·24	60		66	90	26	Unknown.
159	,, 2	0·085	42·5		60	71	27	Unknown.
167	,, 4	0·42	105		63	157	28	Male. aet. 49. Shop assistant.
168	,, 4	0·99	247·5		66	370·5	29	Male. aet. 32. Kitchen porter.
169	,, 2	0·155	77·5		60	129	30	Male. aet. 21. Carpenter's mate.

† S—Shaft. F—Femur. p.p.m.—Parts per million.
LE—Lower end. H—Humerus. * in margin indicates control experiment to which lead has been added.
UE—Upper end. M—Marrow.

‡ *Note.*—The percentage of ash of the bone was determined independently of the lead determination by ashing a known weight of the respective sample of bone, and the results given in column 7 are the values for lead expressed in terms of the ash so determined. This was done in order to ascertain whether the amounts of lead in "normal" bones bore any definite relationship to their inorganic constituents.

TABLE III

ORGANS AND BLOOD*

Exp.	Material analysed Fresh weight Grms.	Lead found, as Pb. Mgrm.	Average amount of lead in fresh tissue p.p.m.	Case No.	Clinical details
66	Blood, 20	0·015	0·33	16	Male. aet. 57. Cook. Broncho-pneumonia. (See Table II, Exp. 80, etc.
67	,, 10	nil			
68*	,, 20 +0·05 mgrm. Pb. added	0·055 −0·05 = 0·005			
69	Liver, 10	0·01	1·8		
70	,, 20	0·015			
72	,, 10	0·025			
71*	,, 10 +0·10 mgrm. Pb. added	0·13 −0·10 = 0·03			
73	Kidney, 10	nil	nil†		
74	,, 20	nil			
76	,, 10	nil			
75	,, 10 +0·05 mgrm. Pb. added	0·03 −0·05 = −0·02			
80	Shaft femur	(See Table II)	112·5		
81	,, ,,				
116	Liver, 10	nil	nil	18	Male. aet. 72. Occupation unknown. Intestinal obstruction. (See Table II, Exp.121, etc.
117*	,, 10 +0·10 mgrm. Pb. added	0·09 −0·10 = −0·01			
120	Kidney 10	0·015			
118*	,, 10 +0·10 mgrm. Pb. added	0·10 −0·10 = nil			
121	Shaft femur	(See Table II)	48·5		
122	,, ,,				
96	Liver, 10	0·015	1·5	17	Male. aet. 3½. No occupation. Acute pulmonary tuberculosis. (See Table II, Exp. 102, etc.)
109	,, 10	0·01			
112	,, 10	0·025			
95*	,, 10 +0·050 mgrm. Pb. added	0·035 −0·05 = −0·015			
05*	Liver, 10 +0·05 mgrm. Pb. added	0·07 −0·05 = 0·02			
108*	Liver, 10 +0·10 mgrm. Pb. added	0·105 −0·10 = 0·005			
97	Kidney, 10	0·015	1·25		
115	,, 10	0·020			
98*	,, 10 +0·05 mgrm. Pb. added	0·055 −0·05 = 0·005			
114*	Kidney, 10 +0·10 mgrm. Pb. added	0·11 −0·10 = 0·01			
102	Shaft femur	(See Table II)	29		
103	,, ,,				

TABLE III—*continued.*

Exp.	Material analysed Fresh weight Grms.	Lead found, as Pb. Mgrm.	Average amount of lead in fresh tissue p.p.m.	Case No.	Clinical details
130	Liver, 10	0·01	1·5	19	Male. aet. 65. Occupation unknown. Broncho-pneumonia. (See Table II, Exp. 129, etc.)
128*	,, 10 +0·10 mgrm. Pb. added	0·12 −0·10 = 0·02			
129	Shaft femur	(See Table II)	50		
131	,, ,,				
134	Blood, 20	0·01	0·5	20	Female. aet. 38. Housewife. Heart failure. (See Table II, Exp. 140, etc.)
149	Liver, 10	0·01	1·5		
148*	,, 10 +0·30 mgrm. Pb. added	0·32 −0·30 = 0·02			
132	Kidney, 10	—	2·0		
138	,, 10	—‡			
141	,, 10	—			
144*	,, 10 +0·05 mgrm. Pb. added	0·07 −0·05 = 0·02			
145*	Kidney, 10 +0·25 mgrm. Pb. added	0·27 −0·25 = 0·02			
140	Shaft femur	(See Table II)	44		
153	,, ,,				
164	Blood, 100	0·06	0·6	21	Male. aet. 40. Occupation unknown. Head injury.

* in margin indicates control experiment with added lead.
† Yellow colour, but readings possible.
‡ Yellow colour, readings impossible.

TABLE IV

URINE AND FAECES*

Exp.	Material analysed	Lead found as Pb. Mgrm.	Average* Mgrm.	Lead p.p.m.	Case No.	Clinical details
22	Urine, 500 ml.	0·145	0·135	0·27	22	Male. aet. 36. Telephone cable engineer. Blue line on gums. Extensor weakness.
23	,, 500 ml.	0·13				
24*	,, 500 ml. +0·10 mgrm. Pb. added	0·23 −0·10 =0·13				
63	Urine, 500 ml.	0·04		0·08	23	Male. aet. 40. Occupation unknown. Indefinite symptoms.
154	Urine, 500 ml.	0·07	0·06	0·12	24	Male. aet. 60. Plumber. Lead colic. Blue line on gums.
155	,, 500 ml.	0·05				
162	Dried faeces, 2 grms.	0·05	0·105 (for 4 grm.)	26·25 (dried faeces)	25	Male. aet. 27. Student. No symptoms.
163	,, ,, 4 grms.	0·11				

* in margin indicates control experiment with added lead.

Discussion.—The material used in these experiments was taken from *post-mortem* cases at St. Mary's Hospital and from patients attending for treatment. Some were cases of sudden death, due to accident or disease, in which a complete history could not be obtained, but in others it was possible to elicit information regarding occupation, illness, etc. In none of the cases, excepting the three whose urines were examined, was any exposure to lead discovered beyond the every-day hazard. So far it has not been possible to obtain bone or teeth from an established case of plumbism.

Bone.—From a study of Table II it will be observed that we have never failed to detect lead in any of the twenty bones examined, and that the amounts of lead present vary from 14·5 to 146·0 p.p.m. of fresh bone (which is equivalent to 25·5 to 232 p.p.m. of ashed bone); 25 per cent. of these cases have a lead-content of over 100 p.p.m. of fresh bone.* Our results for lead in teeth in the five "normal" cases examined are 42·5 to 247·5 p.p.m. of fresh specimen (71 to 370·5 p.p.m. of ash). These figures (for bone and teeth) are considerably higher than those given by other workers in this field, *e.g.*

	Amount of lead detected
Aub, Fairhall, Minot, Reznikoff (*Lead Poisoning*, 1926, p. 56).	
Specimens of bone from 26 "normal" cases examined; lead found in 17.	0·9 to 20·8 p.p.m. fresh bone.
Bone from 7 cases of plumbism.	21·7 to 153 p.p.m. fresh bone.
Barth (*Virchow Arch. path. Anat.*, 1931, **281**, 146).	
Bone from 40 "normal" persons. Lead found in all cases.	10 to 60 p.p.m. ashed bone.
Jowett, Dilling, Bell (*Lancet*, 1929, i, 126).	
Bone from patients treated for carcinoma with colloidal lead injections.	4 to 53 p.p.m. (? fresh) bone.
Animals experimentally lead-poisoned.	Up to 100 p.p.m. whole bone (? fresh).
Danckwortt and Jürgens (*Arch. Pharm.*, 1928, **266**, 492).	
Dogs experimentally lead-poisoned. (Cranium most lead, bones of limbs least, ribs intermediate.)	8·4 to 51 p.p.m. (? fresh) bone.
Tannahill (*Australian Med. J.*, 1929, **1**, 216).	
Bone from two lead workers.	32·5 and 652 p.p.m. (? fresh) bone.
Weyrauch (*Z. Hyg. und Inf.*, 1930, **111**, 162).	
Bones of rabbits experimentally lead-poisoned.	10 to 23·3 p.p.m. fresh bone.
Pfrieme (*Arch. Hyg.*, 1934, **232**).	
Teeth from 60 "normal" persons. Lead found in all.	23 to 73 p.p.m. ashed teeth.
Teeth from 3 cases of plumbism; average.	140 p.p.m. ashed teeth.
(Lead found in teeth of normal and experimentally lead-poisoned animals.)	

The discrepancy between our results for "normal" bones and teeth and those of other workers may be due to a higher lead-content of the bones examined by us or, as we think more likely, to our method of analysis which, by the avoidance of ashing of the organic matter and by the use of diphenylthiocarbazone to extract the lead, gives more accurate results. We have found that bone is very refractory to ashing at temperatures about 500° C., and we suspect that many workers may have lost lead at this stage of the process on account of ashing for prolonged periods at high temperatures; alternatively, incomplete ashing would result in the persistence of some residual organic matter upon which the lead might readily be adsorbed and consequently lost.

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* The highest figure for lead in bone was obtained from Expts. 64, 65, *viz.* 451·5 p.p.m. of ashed bone. (See note to Table II.)

It is stated in a recent publication (Leschke, *Clinical Toxicology*, 1934, p. 10) that most of the lead is stored in the bone marrow. We have not found this to be so in our cases, our figures for marrow being 23 to 50 p.p.m. The results of Aub and his co-workers (*loc. cit.*, p. 69) agree with ours, and they state in their exhaustive work on this subject (Chap. XI) that the anaemia of plumbism is due to peripheral destruction of red blood cells, and not to a local action of lead on the bone marrow. Investigation of bone marrow is complicated by the fact that it is difficult to obtain uniform samples.

In a number of femora examined the lead-content of the ends, as well as of the shaft and the marrow, was determined. Here, again, it was found difficult to obtain uniform samples, as the ends are composed of cancellous bone which, unlike compact bone, cannot be uniformly sampled after crushing, owing to expression of oily marrow. On this account portions were split off from the ends of the bone and subjected to analysis without removal of the marrow.

The results obtained from analysis of the ends of bone do not permit of any significant conclusions, although in nearly all cases the lower end was found to contain more lead than the upper end. When expressed in terms of ashed bone, the ends almost always have a higher figure than the shaft. The difference between the lead-content of the upper and lower ends and the ends and the shaft is probably to be explained by the way in which growth of bone takes place in relation to the epiphyseal lines and to the periosteum, and also to the association between deposition of lead and calcification. It has been demonstrated radiologically (Rogers, Peck, Jupe, *Lancet*, 1934, II, 29; Waters, Kaplan, *Year Book of Radiology*, 1932) in clinical and experimental cases of plumbism that in growing individuals lead produces a subcortical sclerosis most marked at the ends of the bones, and at the epiphyseal lines where growth is most active, and where calcium and any circulating lead is being deposited under normal conditions. To discuss the disposition of the epiphyseal lines and their duration would be out of place here, and it will be sufficient to point out that if an individual is exposed to lead in early youth while bone-growth is most active at the ends, these will probably be found to contain relatively more lead than the shaft (if bone from the actual region of the epiphyseal line is analysed, as has been done with the lower end and not with the upper end). On account of the practical difficulties of obtaining uniform specimens of marrow and ends of bone only a few such analyses were made.

In three cases the lead-content of the shaft of the humerus was determined, as well as that of the shaft of the femur; the former was found in every case to contain slightly less lead than the latter. Danckwortt and Jürgens (*loc. cit.*) give the following figures from experimentally lead-poisoned dogs:—Bones of limbs, 8·4; ribs, 46; skull, 51 p.p.m. (fresh bone). Although these figures are open to question by reason of the method of analysis used, they do suggest that the lead-content of different bones varies.

It is, perhaps, worthy of note that the total amount of lead in the bones may reach considerable proportions. If we take, for example, a 12-stone man who has

100 p.p.m. of lead in his bones, he will have in his whole skeleton 7·6 grms. (117 grains) of lead (as Pb), or 9·9 grms. (153 grains) of lead phosphate, $Pb_3(PO_4)_2$. Lead stored in the bones remains there under normal conditions in a harmless form. In cases of chronic plumbism or after prolonged exposure to lead, when the amount of lead in the bones may be assumed to be much higher than our figures show, mobilisation will aggravate the existing condition, or may give rise to definite symptoms of plumbism. Such mobilisation may result from a number of causes, *viz.* medication, changes in diet, pathological conditions, *e.g.* disturbance of calcium metabolism, acute infections, shock, starvation, etc. These may produce small changes in the hydrogen-ion concentration of the blood, which presumably affect the stability of the tertiary phosphate.

OTHER BIOLOGICAL MATERIALS.—It will be observed that in only a comparatively few cases have organs and blood been analysed, the reason for this being that we were more concerned with the applicability of the method to these substances than to the actual amount of lead present in them. Our figures show that traces of lead are present in organs and blood from "normal" persons.

When applied to organs the method occasionally gave rise to difficulties. Wet oxidation, although troublesome in some cases, did not offer any real difficulty, and extraction of the lead was easy. It was found, however, that in some cases, after oxidation of the diphenylthiocarbazone residues, a yellowish colour persisted, which made the colorimetric reading either impossible or unreliable. It will be noted from the Tables that there is considerable variation in results for organs, and that added lead is not always completely recovered; this error doubtless arose on account of the difficulty of making accurate readings in the presence of this colour. What this interfering substance is we do not know definitely (it may be some very resistant fatty substance which is extracted by the chloroform), and we have not as yet devised a method for its removal. This yellow colour may be due to the presence of nitro-bodies which are resistant to further oxidation by nitric and sulphuric acids. (Since this work was completed it was suggested to us that treatment with ammonium oxalate might destroy the colour.)

The method, when applied to blood, was also found to be rapid and simple, even when a large quantity was used, *e.g.* 100 ml. The amount of lead found in the 100-ml. specimen of blood examined (Expt. 164), *viz.* 0·06 mgrm. per 100 ml., or 0·6 p.p.m., is significant, because, whilst this was a "normal" case, the lead-content of the blood is above the normal range given by Litzner and Weyrauch (*Med. Klin.*, 1933, **29**, 381), *viz.* up to 0·04 mgrm. per 100 ml.

When applied to urine the method was found to be very satisfactory, although the oxidation process may occasionally prove to be tedious. The amounts of lead found in the three cases examined (Table IV) compared with the limits of lead in "normal" urine, given by Francis, Harvey and Buchan (*loc. cit.*), *viz.* up to 0·133 mgrm. per litre, are in accordance with the clinical findings in our cases.

The analysis of the specimen of faeces by this method presented no difficulty.

SIGNIFICANCE OF ANALYTICAL FINDINGS.—The presence of a high lead-content in bone is not in itself evidence that the lead was a contributing factor in the cause of death, but is a "silent witness" of exposure to, and absorption of, lead at some stage or other. It must be remembered that lead, after reacting with the tissues and causing damage, does not remain there, but is removed by the blood-stream, and either excreted or stored in the skeleton. This explains the failure to find lead in certain tissues, *e.g.* brain in lead encephalopathy, after fairly definite evidence clinically of lead poisoning, and in such cases determination of lead in the bones would doubtless be of great value. It must also be remembered that the kidney which is damaged by nephritis may fail to excrete the lead circulating in the blood, and this again may be a possible cause of failure to detect excess of lead in the urine in some cases of plumbism; in such a case analysis of the blood for lead might be of use. A spectrographic method of blood analysis has been used with success by Shipley Scott and Blumberg (*Bull. Johns Hopkins Hosp.*, 1932, **51**, 327) in the diagnosis of plumbism in children.

The diagnosis of lead poisoning at autopsy is notoriously difficult, owing to the lack of positive evidence, and in the living subject it is often largely a matter of guesswork. It has been our endeavour to elaborate a technique for the accurate determination of lead in bone and other tissues, and to set forth the "normal" figures which may be found. These may require modification when further information is available, but we trust that they may be of assistance in the study and the diagnosis of chronic lead poisoning.

SUMMARY.—An accurate and comparatively simple method for the determination of lead in bones has been devised. The process involves wet oxidation (instead of ashing), followed by diphenylthiocarbazone extraction of the lead and subsequent colorimetric determination as sulphide. Special precautions must be taken to exclude bismuth, if present. By the use of this method we have found that the limits of lead in a series of twenty "normal" bones are 14·5 to 146·0 parts per million of "fresh" bone, and in teeth from five "normal" persons 42·5 to 247·5 parts per million of "fresh" teeth. These figures are considerably higher than those given by other workers.

The method has been successfully applied to other biological material (marrow, organs, blood, urine and faeces).

We desire to express our thanks to the Pathological Department, St. Mary's Hospital (Director: Dr. W. D. Newcomb) for a supply of *post-mortem* material. One of us (T. G. O.) is indebted to the Pathological Institute of the Hospital for the award of a Research Studentship which has enabled him to take part in this work.

DISCUSSION

Sir WILLIAM WILLCOX congratulated the Society on the very valuable work that it was doing, particularly in relation to toxicology. As Senior Physician at St. Mary's Hospital, he could testify that papers published in THE ANALYST had been of very great value in clinical medicine. The present paper by Dr. Roche Lynch and his co-workers would upset many of their preconceived ideas. Bone had not been systematically investigated in toxicology, and it was difficult to find in the literature any really reliable information about metals being deposited in bones; the statements in textbooks had been copied from one to another for many years.

The question of lead was very important and difficult; he was constantly being faced with it in clinical work. As they knew, under the Workmen's Compensation Act, a person suffering from lead poisoning received higher compensation than he could otherwise obtain; the result was that when workmen were ill they hoped that some doctor would diagnose lead poisoning. Such a diagnosis might tend to prevent a patient ever doing any work again. He had recently had a case in which a man's illness five years previously had been diagnosed as lead poisoning, but the man showed no clinical indications of it now, and it was doubtful whether he had ever suffered from it. The problem came before the Departmental Committee appointed three or four years ago to enquire into the possibility of danger from the use of lead ethyl, and it was found, when the analytical figures were considered, that lead was present in normal persons. It was most interesting to find that the authors' investigation showed that relatively high amounts of lead were normally present in the bones. The quantity taken into the system must have been appreciable, and the authors appeared to suggest that it was stored in the bone in an innocuous form. The quantities now recorded were much higher than those found by other chemists, which was doubtless due to the greater accuracy of the method of determination. It was very difficult to disprove in Court the possibility of lead poisoning. In a recent case amounts of lead much lower than those found by the authors for normal persons had been determined in the faeces, and the illness had been diagnosed as lead poisoning.

The new method should prove a valuable test for certain clinical diagnoses. The authors had given certain figures for the amount of lead in the blood of a person not exposed to lead; he had no doubt that the blood of persons exposed to lead poisoning would be much greater. The behaviour of calcium was most important in connection with many diseases of which little was known. If parathyroid extract were injected into the veins, it mobilised the calcium; it would be a most interesting experiment if Dr. Roche Lynch would determine the lead in the blood of a normal person, then give parathyroid and see if the lead increased. If lead behaved in the same way as calcium, there should be considerable increase.

Dr. S. A. **Henry** also congratulated the authors. Regarding the question of controls, he was never quite sure what was meant by a "normal" person. Where did this lead come from in a so-called "normal" person? As far as possible, apparently by the history, lead from drinking water had been excluded; did it come from food, or to what extent was it present, normally, in the body? Had the authors, for instance, found any present in the new-born child? He assumed that, so far as bones were concerned, the presence of lead found post mortem must be evidence of chronic absorption—not necessarily of lead-poisoning—as the two conditions should be distinguished. How far would it be possible to use this method for examination of excreta in cases of acute lead-poisoning? With reference to the large amount of lead in faeces, the statement that in cases of lead-poisoning it was useless to examine the faeces for the first week or so was of practical importance. Was the lead found, in the cases under consideration, ingested or inhaled? Inhalation was the most important cause of lead absorption and poisoning in industrial cases.

Professor W. H. **Roberts** added his congratulations. He asked why the authors had confined themselves to the use of nitric and sulphuric acids in oxidising the bone. He had oxidised urine with nitric acid and potassium chlorate, and found it a very quick and very good method. The lead had then been extracted by the electrolytic process. Had the authors ever tried this method? He had also found it successful for the determination of lead in livers, etc. In one case of suspected lead-poisoning he had found only 0·12 p.p.m. in the liver—an amount which Dr. Roche Lynch had found in a normal person. On the other hand, he had found ten to twelve times this amount in cases of chronic lead-poisoning. He would certainly test the process thoroughly, as it might be much simpler in practice than it appeared, although he did not like oxidising with nitric and sulphuric acids every time. When there was plenty of material available it would be well to use both methods. In cases of suspected chronic lead-poisoning, it seemed that it would be a good idea to get the patient into hospital, draw some of his teeth, analyse them and thus settle the matter once and for all. He had always had difficulty in stating in evidence the amounts of lead normally present, and, in giving these, the paper was a very valuable contribution to the subject.

Mr. J. R. Nicholls, adding his congratulations, especially with regard to the neat way of overcoming the interfering effect of such large proportions of calcium phosphate, said that Dr. Roche Lynch had rightly stressed the fact that the solution to be extracted must be perfectly clear. How was this to be ensured in all cases? If the final solution contained traces of iron phosphate or magnesium phosphate, the liquid might appear clear to the eye and yet might have a very slight turbidity sufficient to adsorb lead and prevent its extraction. Also, small quantities of aluminium might similarly interfere. Some caution was therefore needed before the process was adopted as a general method.

Mr. A. L. Bacharach welcomed the work that had been presented, partly because it put an important instrument into the hands of biochemists for investigating the metabolism of lead. It should now be possible to conduct the essential preliminary animal experiments by making use of a diet significantly free from lead, for the methods brought before the Society would enable the necessary analyses of foodstuffs to be made with an accuracy previously unobtainable. It would be possible to add to this lead-free diet small or large quantities of lead, with a view to examining the rate of storage and the method of excretion. It would be important to discover to what extent the kidneys could "take care of" lead, and whether there was any significant variation in the time taken by different individuals to get rid of lead. It might be that varying susceptibility to lead poisoning was due to variation in the efficiency with which the metabolic machinery of different individuals could cope with excess lead. The matter was one of importance in the veterinary as well as in the clinical field, because of the well-known abortifacient action of lead and the prevalence of habitual and other forms of abortion among domestic animals.

Dr. Osler, replying to Dr. Henry's questions about lead in the bones of infants, said that he had had a case of a male, 3½ years of age, the shaft of whose femur contained 29 parts per million of lead. Infants obtained their calcium from their mothers, and he thought that the same applied to lead. The diagnosis of plumbism still remained a clinical question. He had used this method in several cases of lead-poisoning, and it had worked very well indeed, the results being in accordance with the clinical findings. With regard to the lead in the faeces of the student investigated being due to inhalation or ingestion, he knew the student personally, and he had not been exposed to inhalation of lead; in all probability he had derived the lead by ingestion in his lodgings, *e.g.* from solder in a frying-pan.

The reason why it was useless to examine the faeces for lead from a case of suspected lead-poisoning during the first week or so after removal (*e.g.* to hospital) from the source of the lead was because the lead present in these specimens might be due to ingestion of lead alone. After some time had elapsed any excess of lead found in the faeces might be taken with more or less certainty to arise from the excretion of previously-absorbed lead.

Replying to Professor Roberts, Dr. Osler said that he had not tried the potassium chlorate and nitric acid method of oxidation or the electrolytic method of separating lead.

With regard to the question, raised by Mr. Nicholls, of the interference of certain substances, Allport and Skrimshire had found that it was possible to avoid the interference of most of the substances in the long list of those which they had tested. So far as he and his colleagues could find, there were no interfering substances in their experiments.

Mr. Bacharach had referred to the amount of lead that the kidneys could excrete. It had been found by Aub and his co-workers that the maximum quantity excreted in the urine in lead-poisoning was not very great, and that most of the lead was excreted in faeces.

The question of abortion in animals had many points of interest, and he thought that Mr. Bacharach was quite right in saying that abortion might somehow or other be associated with lead, because of its known action upon the sexual organs. The wives of workers in factories where lead was extensively used were rather liable to abortion, but this tendency ceased when the workers changed their occupation. When deer grazed upon lead-contaminated fields the growth of their antlers was affected, and chickens kept on the same land had been known to lay addled eggs. Lead had a very definite harmful effect upon animals.

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The Composition of the Amniotic Fluid

BY ARNOLD R. TANKARD, F.I.C., D. J. T BAGNALL, F.I.C., AND F. MORRIS, F.I.C.

(Read at the Meeting of the North of England Section, October 13, 1934)

WE were concerned recently in a case in which it was alleged that a person had attempted to procure the abortion of a woman who had been pregnant for about 5 months. We made an examination of the amniotic fluid for the presence of abortifacients and other drugs, but these were not detected. We were also required to say whether the fluid had been diluted by admixture with soap solution or water, and our answer to this question was also in the negative. It thus appeared that we were dealing with a normal fluid, the composition of which may not be without general interest; for, although there are some analytical figures in the text-books, these are rarely of recent date and are also incomplete.

The following table gives some of the published results of analyses of the amniotic fluid:

	Hoppe-Seyler[1] Per Cent.	Landois and Starling[2] Per Cent.	A. L. Galabin[3] Per Cent.	J. C. Webster[4] Per Cent.
Total solids	1·6	0·5 to 2	—	Less than 2
Water	98·4	—	—	—
Albumin	0·2	0·1 to 0·33	0·08 to 0·8	Trace Albumin and globulin
Extractives	0·8	—	(Urea) trace to 0·4	—
Dextrose	—	Present	—	Trace
Salts	0·6	—	—	—
Sp.gr. at 15·5 °C.	—	1·007–1·011	1·004–1·025 (1·010 at end of term)	1·002 to 1·028 (aver. 1·008)
Reaction	—	—	slightly alk. or neutral	Slightly alk. or neutral
Normal quantity	—	1 to 2½ pints	—	1 to 2 pints

[1] Green's *Encyclopaedia of Medicine and Surgery*, 1900, Vol. III.

[2] *Text-Book of Human Physiology*, Vol. II, 4th Edition (1891), p. 1064. These authors state that the fluid contains also mucin, globulin, a vitellin-like body, urea, ammonium carbonate (from decomposition of urea), calcium sulphate and phosphate, sodium chloride, and sometimes lactic acid and creatinine.

[3] *Manual of Midwifery*, 3rd Edition (1893), p. 60. The percentage of albumin is stated to decrease, and that of urea to increase, as the pregnancy advances.

[4] *Text-Book of Obstetrics*, 1903, p. 89.

According to Halliburton,* the amniotic fluid is believed to have its origin as a simple exudation from the tissues of the foetus. After the formation of the placenta, however, a transudation of lymph takes place from the maternal vessels (Jungbluth). Later it becomes mixed with foetal urine (Gusserow), and, in common with urine and blood, contains proteins, urea and salts, in addition to water. The normal quantity of fluid is from one to two pints. Sometimes, however, the amount is abnormally small, and sometimes abnormally large (hydramnion). In the latter case the proteins are said to be more abundant than in the normal fluid.

Schäfer states that there is 0·06 per cent. of fat in amniotic fluid. Webster (*loc. cit.*) quotes Veit as saying that the freezing-point of this fluid is always higher than that of the foetal or maternal blood, but no figures for this determination are given.

The fluid examined by us was collected in two portions; it had a total volume of 525 ml., or about 18½ fluid ounces, and gave the following results on analysis:

	1	2
Appearance	Cloudy. Pale straw colour	Yellowish. Trace of blood present
Sp.gr. at 15·5° C.	1·0091	—
	Per cent. (w/v)	Per cent. (w/v)
Total solids	1·5	1·6
Mineral matter (ash)	0·72	0·72
Total chlorine as NaCl	0·66	0·66
Albumin	0·3	0·4
Urea	0·18	0·21
Acidity to phenolphthalein (ml. *N*/10 alkali per 100 ml.)	8·0 ml.	9·0 ml.
p_H value	about 7·0	
Freezing-point (Hortvet) °C.	−0·550	−0·557

The albumin was determined approximately by centrifuging a known volume of the fluid, after the addition of the picric acid reagent, in an Aufrecht's albuminometer. The urea-content was ascertained by the volumetric hypobromite method. The reaction of the fluids to litmus was neutral.

It is interesting to observe that the freezing-point of this fluid, before it is diluted with foetal urine, is what would be expected from a knowledge of the characteristics of other normal animal body fluids, and the figures obtained under this head confirmed us in our opinion that the fluid had not suffered any appreciable dilution or admixture with extraneous liquids.

ADDENDUM.—Since the reading of this paper we have had the opportunity, through the kindness of Dr. N. Gebbie, Medical Officer of Health for the City of Hull, of consulting recent medical literature on this subject, and in particular two papers—one by Shrewsbury, "Observations on the Chemistry of the Liquor Amni" (*Lancet*, 1933, **224**, [i], 415); the other by Makepeace, Freemont-Smith, Dailey and Carroll, "The Nature of the Amniotic Fluid" (*Surgery, Gynaecology and Obstetrics* [Chicago, U.S.A.], 1931, **53**, 635). The first-mentioned paper deals chiefly with the chemical composition of the amniotic fluid in the presence of maternal disease. The second paper is a comprehensive and comparative study of the composition of the human amniotic fluid and maternal blood-serum. The following figures are given for the freezing-point depressions of these fluids, the determinations being made in the Beckmann cryoscopic apparatus, using a

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* *Text-Book of Chemical Physiology and Pathology*, 1891, p. 354.

Heidenhain thermometer and a mechanical stirring device (Findlay, *Practical Physical Chemistry*: Longmans, Green & Co., London, 1923, p. 112):

	Fluids at term			Fluids before term	
	Serum °C.	Amniotic fluid °C.		Serum °C.	Amniotic fluid °C.
Highest	−0·573	−0·540		−0·589	−0·562
Lowest	−0·526	−0·463		−0·539	−0·506
Average (of 21 cases)	−0·551	−0·502	(of 15 cases)	−0·557	−0·539

Summarising their results, the authors of this paper state: "The amniotic fluid contains small amounts of a fermentable reducing substance which is undoubtedly glucose. It contains creatinine, or creatinine-like substances, in slightly greater concentration than the maternal serum. Its protein-content varies from 105 to 502 mgrms. per 100 c.c. at term. It has slightly less sodium and usually slightly more chloride than maternal serum at term. In the earlier months of pregnancy the chloride in the amniotic fluid is always greater than that of the maternal serum. At term the amniotic fluid is distinctly hypotonic to maternal serum, but in the earlier months of pregnancy this hypotonicity is less, and in the earliest months the amniotic fluid may be isotonic with maternal serum. Thus, early in pregnancy the amniotic fluid approaches the composition of other protein-poor fluids which are in osmotic equilibrium with the blood-plasma. This suggests that the amniotic fluid originates as a dialysate in equilibrium with the maternal and foetal body-fluids. The foetal urine is definitely hypotonic, and is present in the bladder as early as the fourth month in pregnancy. This indicates that, as pregnancy advances, the amniotic fluid becomes more and more diluted by the hypotonic foetal urine."

Caution should therefore be exercised in making deductions from the results of freezing-point determinations on this fluid, owing to its possible dilution with foetal urine. In our case, the freezing-point figures decidedly negative any appreciable dilution, either by foetal urine or other fluid introduced from outside. It seems clear that the amniotic fluid will usually be undiluted, and will show a normal freezing-point, as an unmixed body fluid, up to five months of pregnancy, after which, the amount of urine from the foetus may become appreciable, with a consequent smaller freezing-point depression. The foetal urine, in two cases recorded by Makepeace and his colleagues, showed freezing-points of −0·141° and −0·174° C. (Beckmann), with sodium chloride-content of 0·14 and 0·17 per cent. w/v, respectively.

THE HULL CITY LABORATORIES

Determination of Impurities in Commercial Carbon Monoxide

By H. R. AMBLER, Ph.D., B.Sc., F.I.C., and
T. CARLTON SUTTON, M.A., M.Sc., F.Inst.P.

The precise determination of the composition of carbon monoxide has become increasingly important on account of the use of this gas in industrial research. During a search for a gaseous mixture which could be used as a standard for determining the thermal capacity of high-pressure calorimetric apparatus we have met with the same problem. A technique developed for this analysis, and the results obtained for the contents of a typical cylinder of the gas, are described below.

Separate samples were used for the measurement of small quantities of the following gases which were present as impurities: (i) hydrogen, methane and nitrogen (including argon), (ii) oxygen, (iii) carbon dioxide, and (iv) carbonyls.

(i) Hydrogen, Methane and Nitrogen.—About 125 ml.* of gas from the cylinder were shaken with 10 ml. of ammoniacal cuprous chloride solution until some 90 per cent. of the volume was absorbed. As the partial pressure of the residual gases now amounted to approximately 0·05 atmosphere, the volume of the absorbent was reduced to 1 ml., and the shaking was continued. In addition to absorbing the carbon monoxide, the solution absorbed small quantities of the impurities; with this procedure, however, the volume of the latter absorbed did not exceed 0·05 ml., *i.e.* 0·04 per cent. of the total gas, or 8 per cent. of the 0·5 per cent. of residual gas.† Alternatively, and more conveniently, a bubbling pipette may be used, care being taken that the gas is passed at such a rate that the absorption is not complete and the partial pressures of the impurities do not become high when the top of the absorbent column is approached.

It was thus assured that the residual gases contained substantially the whole of the hydrogen, methane, nitrogen and argon present in the original gas, together with a diminished proportion of the carbon monoxide.

This residual gas was analysed in an apparatus[2] described in 1929. It was shaken with successive quantities (see Table II) of ammoniacal cuprous chloride solution to remove the last traces of carbon monoxide[3]; the volume (about 0·5 ml.) was then measured. Sufficient air was added to reduce the hydrogen-content below 5 per cent.,‡ and the mixture was passed into a chamber containing a platinum spiral heated to barely visible redness. Here the hydrogen was burned and the methane was left unaffected.[4] By treating the gas with alkali at this stage, a proof was provided, both that methane was unaffected and that carbon monoxide was absent in the immediately preceding stage. After measurement of the volume, combustion of the methane was effected by heating the wire to bright yellow; agreement between the observed contractions (i) after combustion and (ii) after absorption of the carbon dioxide formed on combustion, indicated that the analysis was satisfactory. Further checks can be obtained by determining the amount of oxygen consumed in each of the combustions.

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* In one test, 450 ml.

† Solubility of nitrogen in 1 volume of water and at 1 atmosphere partial pressure 0·018 vol.

‡ With small quantities of gas (1 ml.) the amount of hydrogen which can be burned without heating the wire unduly is as high as 7 per cent.

The results of triplicate determinations of these constituents in the gas are given in Table I, and an example of the detailed measurements from which these are calculated is given in Table II.

TABLE I

DETERMINATIONS OF NITROGEN, HYDROGEN AND METHANE IN A CYLINDER OF CARBON MONOXIDE

		Triplicate analyses		
Vol. sample taken, ml.		123	129	450
Residue after treatment with cuprous chloride (ml. total)		0·75	0·68	2·38
Percentage composition of gas after treatment with cuprous chloride	Hydrogen	26·0	26·0	28·0
	Methane	2·5	3·0	2·5
	Nitrogen*	71·5	71·0	69·5
Percentage of above impurities in original gas	Hydrogen	0·16	0·14	0·15
	Methane	0·016	0·015	0·013
	Nitrogen*	0·43	0·37	0·37

* A precise measurement of the nitrogen is seldom required, and no attempt has been made to develop methods for measuring it with the same accuracy as the other constituents.

OXYGEN.—The oxygen was determined in a separate sample of the original gas by the pyrogallol colorimetric method recently described[5], and was found to be less than 0·01 per cent.

TABLE II

SPECIMEN OF DETAILED MEASUREMENTS FROM WHICH TABLE I IS CALCULATED

	Pressure (corrected for water vapour) cm. Hg	
Original volume of gas		123·4 ml.
Volume after contact with 10 ml. cuprous chloride		About 7 ml.
After shaking 1 minute with 1 ml. of fresh[3] cuprous chloride (measured in bulb[2] of 0·95 ml.)	67	
After shaking for 1 minute with 0·5 ml. of freshly-prepared cuprous chloride solution	60·2	Whence residual gases (hydrogen, methane, nitrogen and argon) =0·75 ml. at 1 atm. = 0·61 per cent.
(Further shaking with 0·5 ml. of cuprous chloride solution and subsequently with 0·2 ml. of water would cause a contraction not exceeding 0·5 cm. This maximum would correspond with 0·8 per cent. on residual, *i.e.* 0·004 per cent. on original gas.)		
After adding excess of air (bulb[2] of 4·8 ml.)	80·5	
After fractional combustion with platinum wire at dull red heat for 1 minute[4]	75·7	Whence H_2=0·20 ml. = 0·16 per cent.
After contact with alkali solution	75·7	Whence no residual CO left and no methane burnt.
After combustion with platinum wire at bright yellow heat for 2 minutes	$75{\cdot}0_5$	Whence methane=0·02 ml. = 0·016 per cent.
After contact with alkali solution	$74{\cdot}7_5$	Methane-content confirmed

CARBON DIOXIDE.—A 1-litre bottle was evacuated and filled with a sample of the original gas; 5 ml. of $N/25$ lime-water were added, and the bottle was allowed to stand, with occasional shaking, for about two hours. The contents were then washed into a small flask and titrated with $N/25$ hydrochloric acid (phenolphthalein as indicator). Blank determinations with air freed from carbon dioxide were carried out concurrently. Results, corrected by means of the blank determinations, were 0·012 and 0·011 per cent. of carbon dioxide. (The blank determinations gave 0·006 and 0·012 per cent., respectively, these results being attributed to the action between the lime-water and the glass.)

CARBONYLS.—About 10 litres of the gas were passed at the rate of about 150 ml. per minute through a glass tube heated to 300–400° C.[6] The mirror so formed was dissolved in order to enable colorimetric tests for iron and nickel to be made by the Prussian-blue and dimethylglyoxime[7] methods, respectively. In the analysis in question the iron carbonyl amounted to 10 mgrms. of iron per cb.m. of gas, *i.e.* 0·0004 per cent. of iron carbonyl by volume. Nickel was not found; 0·00005 per cent. of carbonyl would have been detected.

It has been found that the carbonyl-content increases with the time which has elapsed since the cylinder was filled; a similar effect was noted by Bunte and Terres.[8] Figures are given in Table III.

TABLE III

CARBONYLS IN CYLINDERS OF CARBON MONOXIDE

	Iron carbonyl		Nickel carbonyl	
	Iron per cb.m. Mgrms.	Vol. per cent.	Nickel per cb.m. Mgrms.	Vol. per cent.
Cylinder A, tested 3 weeks after filling	3	0·0001	<1	<0·0001
Cylinder B, tested 4 months after filling	10	0·0004	<1	<0·0001
Cylinder B, tested 11 months after filling (over summer of 1933)	40	0·0015	3	0·0001

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RESEARCH DEPARTMENT
WOOLWICH

The Detection and Identification of Metallic Particles in Manufactured Products

By H. C. LOCKWOOD, B.Sc., A.I.C.

(*Read at the Meeting, October* 3, 1934)

A METHOD for the detection of metallic fragments in dust, sand, sludge, etc., depending upon the action of silver nitrate solution, has been described by Ward (ANALYST, 1933, **58**, 28). Some metals, *e.g.* copper, tin, lead, zinc, etc., give rise to the formation of silver "trees," but others, *e.g.* aluminium, nickel, chromium, etc., are unaffected. It seemed possible to extend the idea not only to the detection of metals, but also to their identification. When devising the tests, I had primarily in view the following metals and alloys in general commercial use: iron, tin, lead, zinc, copper, aluminium, nickel, mercury, chromium, brass and solder.

PARTICLES AFFECTED MAGNETICALLY.—Since iron particles are those most likely to occur in manufactured products, they should be looked for first. A small amount of the dry material, prepared as described later, is placed on a microscope slide and mixed with a few drops of water. The cover-glass is gently placed in position, and the slide is examined under a one-inch objective. A small magnet is brought near the slide and moved backwards and forwards, when any particles of iron are readily detected. The movement of the particles may also occur with nickel or cobalt, although the presence of the latter is unusual; the following tests are then applied:

TREATMENT WITH ACID FUMES.—To confirm the presence of iron, a small amount of the prepared material is placed on a microscope slide and exposed to the fumes from a mixture of strong nitric and hydrochloric acids contained in a beaker, the slide being supported about one inch from the surface. To accelerate the action, the beaker may be gently warmed on the water-bath. After 5 to 10 minutes the slide is removed and dried in the water-oven. One drop of potassium ferrocyanide solution is then added, and the cover-glass is placed in position. The presence of iron is indicated by patches of Prussian blue. Copper gives a pink colour and growth.

The presence of nickel is confirmed by treating the slide with acid fumes as described above, and then exposing it to ammonia. The cover-glass is placed on the dry material, and a drop of a saturated solution of dimethylglyoxime is added. Bright red patches are produced in the presence of nickel. Cobalt does not respond to either of these tests.

ACTION OF AURIC CHLORIDE SOLUTION.—The auric chloride reagent should have the following composition, since variations in the amounts of acids present affect the results:—auric chloride ($AuCl_3.2H_2O$), 2·5 grms.; nitric acid (concentrated), 1·5 ml.; hydrochloric acid (concentrated), 1·25 ml.; water to 100 ml.

This reagent gives the following reactions:

METAL	REACTION
Tin	Characteristic formation of purple of Cassius radiating from each particle (see Fig. I). Generally reddish at first, changing to blue at the edges as growth extends. No tree-like growth is produced.
Lead	Rapid tree-like growth, which is black by transmitted or reflected light. After some minutes may be dark brown by reflected light (see Fig. 2).
Solder	Characterised by reactions for both tin and lead (Fig. 3).
Iron	Formation of gas, and for some distance round the nucleus a blue hazy deposit which is pale brown by reflected light. A test with a small magnet should be made.
Nickel	Yellow deposit of gold immediately, and later a moderately slow growth of a gold tree, which is yellow by reflected light (Fig. 4).
Mercury	Thin gold coating round edge visible by reflected light; no growth.
Copper	Very slight hazy growth.
Brass	Very slight hazy growth.
Chromium	No action.
Aluminium	Rapid formation of bubbles of hydrogen and of a small tree-like growth.
Zinc	Slow formation of bubbles and of a small tree-like growth.

In the first section of the above table the presence of lead and copper may be confirmed by exposing a slide to acid fumes, drying it in the oven, and adding 10 per cent. potassium iodide solution. Bright yellow patches surrounding nuclei denote lead. Copper liberates iodine, which will give a blue colour on the addition of starch.

Zinc and aluminium may be differentiated by preparing a slide and adding one drop of lead acetate solution. Zinc gives a rapidly-growing lead tree, which is characteristic for zinc and cadmium. The presence of aluminium may be confirmed by preparing a slide and adding mercuric chloride solution, which, in contact with aluminium, yields free hydrogen. Of the metals under consideration, only aluminium responds to this test.

ACTION OF SILVER NITRATE.—In applying Ward's test (*loc. cit.*), a few drops of *N*/10 silver nitrate solution are added to the prepared material on a slide. Tree-like growths, identical in type (see Fig. 5), are given by copper, zinc, solder and brass. Tin gives a distinctive growth, as is shown in Fig. 6. Mercury gives a very slow growth, characterised by appearing silvery white in reflected light. Iron, aluminium, nickel and chromium are generally unaffected. Ward states that tin is sometimes inactive. Iron is active if the material is treated with copper sulphate, so as to form a deposit of copper on the iron.

PREPARATION OF THE MATERIAL.—Before testing for metallic particles it is essential to remove any fat or finely divided matter which would obscure the reactions. This is readily accomplished by sedimentation, with ethyl ether as a solvent. The tube, about 5 inches long by ¾ inch internal diameter, is open at both ends and is tapered to ½ inch at one end. The tapered end is closed with a cork carrying a narrow glass tube fitted with a rubber tube and pinch-clip. The glass tube is made to slide in the cork, so that it can be adjusted to the level of the top of the sediment. From 2 to 5 grms. of material are shaken with ether and transferred to the sediment-tube, the glass tube of which is pushed in about half an inch. The mixture is well stirred and allowed to settle for 2 to 5 minutes, according to the state of division. The pinch-clip is removed and, when the ether has run off, the glass tube is adjusted to the level of the top of the sediment, thereby removing as much as possible of the dissolved and suspended matter in each washing. A fatty material is extracted in this way three times with ether and once with alcohol, followed by two washings with water to remove water-soluble substances, such as sugar, etc. The residue is then transferred to a porcelain basin with the minimum amount of water, and, as the material settles readily on standing for a few minutes, the excess of water can be decanted. The residue is then dried and is ready for testing.

Various modifications of the above procedure may be used; the method selected should depend upon the nature of the original material. In many cases sedimentation with hot water in a beaker will be found very effective.

IDENTIFICATION REACTIONS OF METALS

The following table summarises the identification-reactions of the various metals studied.*

IRON.—(i) Detected by magnet; *(ii) blue patches with potassium ferrocyanide after treatment with acid fumes; (iii) sometimes no growth with silver nitrate; (iv) auric chloride solution gives bubbles of gas and formation of haze.

NICKEL.—(i) Detected by magnet; (ii) absence of blue colour with potassium ferrocyanide after treatment with acid fumes; (iii) red colour after exposure to acid fumes and ammonia, and addition of dimethylglyoxime solution under cover glass; *(iv) auric chloride gives a gold-coloured tree.

ZINC.—(i) Silver tree with silver nitrate; *(ii) lead tree with lead acetate (also given by cadmium); (iii) hydrogen with auric chloride.

TIN.—(i) Silver tree of characteristic shape with silver nitrate (sometimes tin is inert); *(ii) purple growth with auric chloride.

ALUMINIUM.—(i) Hydrogen with auric chloride; *(ii) hydrogen with mercuric chloride.

COPPER AND BRASS.—(i) Distinctive colour of particles (if large enough) by reflected light; (ii) silver nitrate gives silver tree; *(iii) pink colour with potassium ferrocyanide after exposure to acid fumes; *(iv) iodine liberated on adding potassium iodide after exposure to acid fumes.

LEAD.—(i) Silver tree with silver nitrate; (ii) black tree with auric chloride; (iii) mercuric chloride gives a white deposit or growth; *(iv) after exposure to acid fumes and addition of potassium iodide, a yellow precipitate is produced round nuclei; absence of blue colour on adding starch solution.

SOLDER.—(i) Silver tree with silver nitrate; *(ii) black tree and purple colour with auric chloride; (iii) presence of lead denoted as by test No. (iv) under *Lead*.

MERCURY.—(i) Spheroidal particles may be differentiated from air-bubbles by examination by transmitted and reflected light; *(ii) on pressing cover-glass with the point of a penknife the particles can be made to scatter extremely small droplets; (iii) silver nitrate gives a silver-coloured tree when viewed by reflected light.

CHROMIUM.—(i) No reaction with auric chloride; (ii) when exposed to acid fumes gives bright green spots of chromic chloride.

* Denotes characteristic and confirmatory reactions.

I wish to thank Mr. A. W. Knapp and Mr. J. R. Johnson for their interest and advice, and Messrs. Cadbury Brothers, Ltd., for permission to publish this work, which was carried out in their laboratories at Bournville.

THE LABORATORIES
BOURNVILLE

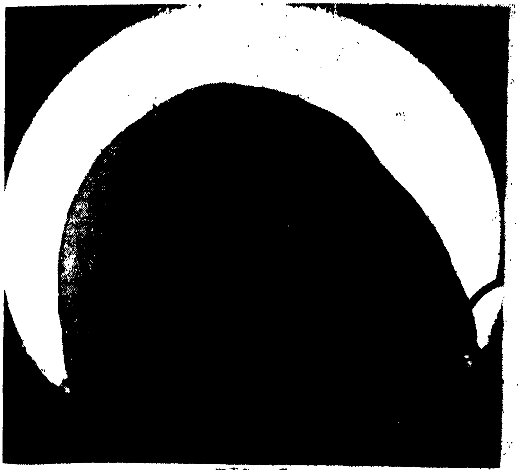

FIG. I

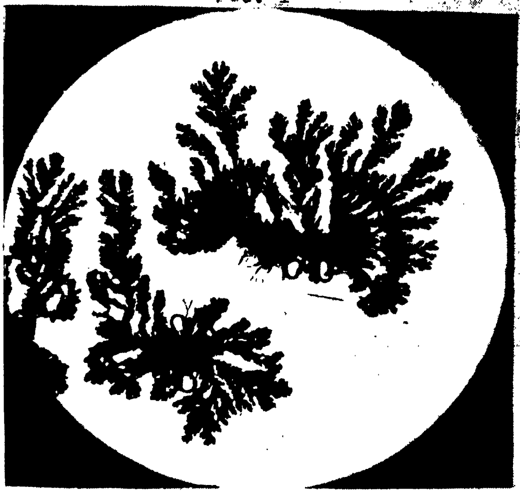

FIG. II

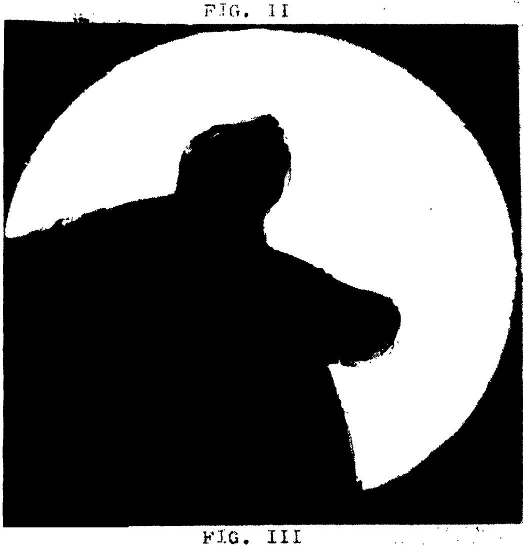

FIG. III

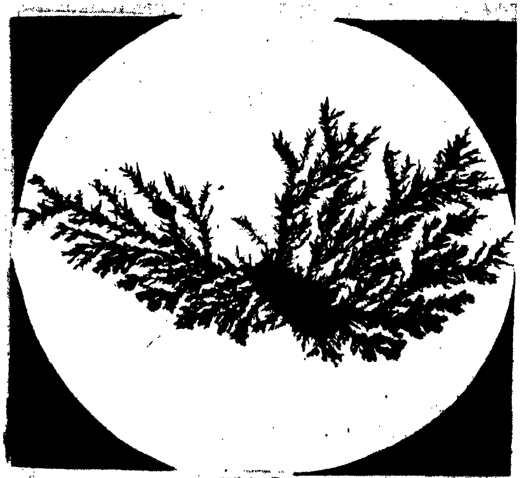

FIG. IV

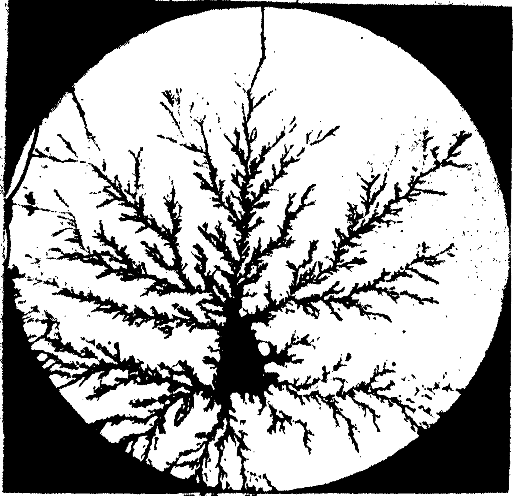

FIG. V

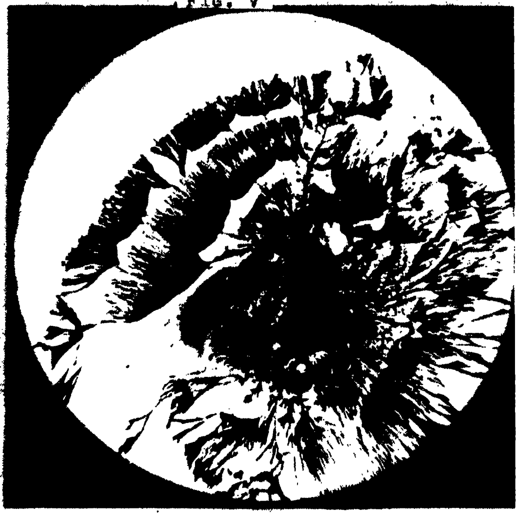

FIG. VI

Notes

The Editor wishes to point out that the pages of the Journal are open for the inclusion of short notes dealing with analytical practice and kindred matters. Such notes are submitted to the Publication Committee in the usual manner.

ULTRA-VIOLET RAYS AS A TEST FOR THE STABILITY OF ANAESTHETIC ETHER

It has long been known that ether intended for anaesthetising purposes should be kept in a cool place in the dark in order to prevent the formation of peroxides. As a test of the effect of heat, such as is experienced in the tropics, we have hitherto subjected ethers, stored in sealed bottles of brown glass, to a temperature of 120° F. for varying periods. Such samples as subsequently remained unchanged on application of the B.P. test for peroxides, were regarded as "stable." Owing to the time involved in carrying out these heat tests, it was desired to find a more rapid method.

More recently, therefore, I have tried the action of ultra-violet rays on Aether Anaesth. P.B. from various sources, and have found that whereas with some samples peroxides developed after this treatment, others gave no reaction in the B.P. test.

The method adopted was simple, rapid and effective. A 1-oz. clean white glass-stoppered bottle was completely filled with the sample and placed for one hour at a distance of about 7 inches from the screen of an ultra-violet lamp (Hanovia lamp of 220 watts), after which it was tested for the presence of peroxides. The glass of the bottle had the following composition:—Sodium oxide, 15·5; silica, 73·7; calcium oxide, 9·0; potassium oxide, 0·4; alumina, 0·8 and ferric oxide, 0·1 per cent. Glass cylinders of 10 ml. capacity (Baird & Tatlock, Ltd.) proved equally effective.

It has been proved that ether stored under normal conditions may satisfy all the B.P. tests for chemical purity, and yet may be affected by ultra-violet rays, and thus cannot be regarded as sufficiently stable to be exported to the tropics. There appears to be a relation between the heat and light tests for stability.

This rapid test should prove useful, and I am indebted to the Directors of Messrs. Howards & Sons, Ltd., for permission to publish it.

S. Gordon Liversedge

NOTE ON FUR DERMATITIS

Some time ago I was called upon to examine a fur, the dye of which was suspected of causing dermatitis. No dye could be extracted, but the fur was decidedly acid, the acid present being sulphuric acid (0·78 per cent.). The fur contained 12·43 per cent. of total solids soluble in boiling water; 7·25 per cent. of these were organic, and 5·18 per cent. inorganic substances, the latter consisting mainly of common salt (4·89 per cent.). Whether the salt had been sprinkled on the fur for the purpose of preserving it or was accidentally present could not be ascertained.

The conclusion was that warm perspiration brought about a reaction between the acid and the salt, and that hydrochloric acid was probably the irritant that had caused the dermatitis.

S. Allinson Woodhead

The Analytical Laboratory
Mountfield Road, Lewes

THE ABSORPTION OF OXYGEN BY PHOSPHORUS

In his paper on this subject (Analyst, 1934, 593) Dr. H. R. Ambler refers to an old controversy between Leeds and Baumann and others concerning the formation of an active form of oxygen other than ozone, by the action of oxygen upon phosphorus. He appears, however, to be unfamiliar with my work on this subject, a record of which appeared in the *Journal of the Chemical Society* for December, 1880. In that investigation, which was conducted to clear up questions previously discussed, it was definitely established that when phosphorus is exposed to the action of air or oxygen in the presence of, or partly submerged in, water under specified conditions, hydrogen peroxide is formed in the aqueous medium, and ozone is produced in the gaseous state.

So far as I am aware, the chemical reactions involved in the process still remain unsolved, although the results are beyond question. To what extent, if any, they may affect Dr. Ambler's modified method of determining oxygen in gaseous mixtures is, perhaps, a matter calling for further attention.

C. T. Kingzett

Weylands
Pyrford Road, West Byfleet

CHEMICAL AND BACTERIOLOGICAL EXAMINATION OF WATER

The question whether, in reporting on a sample of water, reliance is to be put rather on the chemical results or on the bacteriological examination, has, doubtless, presented itself to analysts other than myself. While not claiming to be a bacteriological "expert" or to decide on the presence, in a water, of specific pathogenic organisms, my custom is to give, along with the chemical results, the conclusions also from what may be called a "general bacteriological examination."

To such analysts the narration of a case which recently occurred in my own practice may be interesting.

On making the chemical analysis of a water intended as a public supply I found the results—with the exception of the water being a hard one—to be practically open to no objection whatever. On examination, however, of a separate sample sent in a sterilised bottle, the bacteriological examination was found to be distinctly unsatisfactory, and to show the presence of *B. coli* in considerable numbers. A second sample, sent at my request, gave similar results. Briefly put, I could not, in the face of the chemical analysis (which showed but little organic matter, ammonia, chlorine or nitrates), bring myself willingly to condemn the water on the strength of the bacteriological examination alone. With such unsatisfactory results before me as were yielded by the bacteriological examination, I found myself, however, seemingly obliged to declare the water as not suitable for the purpose of a public supply. Before doing so, however, I made further enquiries, these resulting in the information that the water came from a newly-dug well situated in a pasture field, and over 600 yards away from any farm or dwelling house. The well itself was 23 feet deep, and had been lined with brick all the way down, the top being covered by wooden planks ; the water at the bottom stood at an average depth of 5 feet. I requested the sanitary inspector of the district (for which I act) to procure for me two further samples from the well—the one taken from the surface water and the other from that at the bottom of the well. This latter operation was done by fitting a previously-sterilised bottle in a frame to which a lead weight was attached in order to sink the whole, and provided with a string attached to the stopper, so that the latter could be removed and the bottle allowed to fill completely when submerged and then be drawn up.

Having thus obtained the two samples, the one from the surface, the other from the water as it entered the well, I submitted these to an examination similar to that previously made. Again I found the surface water to give very unsatisfactory bacteriological results, but the sample drawn from the water as it entered the well was entirely satisfactory, showing no *B. coli* whatever, and thus confirming the opinion formed from the results of the chemical analysis previously made.

It was made clear to me, accordingly, that the apparent pollution which showed itself in the earlier bacteriological examinations resulted from something not pertaining to the water itself, but derived, probably, from the bricks or other material used in the construction of the well, and I was able to report accordingly.

It may well be that others beside myself have at different times been in doubt as to whether, when chemical and bacteriological results obtained with a sample of water are not mutually confirmatory, they should decide upon the basis of one or of the other. Not a few of the discrepancies which have occurred may, I feel sure, be explainable in some such way as I have here indicated.

ERIC VOELCKER

1 TUDOR STREET
LONDON, E.C.4

AN IMPROVED METHOD FOR THE ROUTINE DETERMINATION OF FAT IN FAECES

DURING the course of a certain investigation it became necessary to determine the fat-content of a large number of samples of human faeces, it being required to determine fatty acids and soaps as well as unchanged fat. Methods employing previously dried material have been shown (Fowweather, *Brit. J. Expt. Path.*, 1926, **7**, 15) to give low results, mainly because the temperature of drying causes some free fatty acids to become combined. Freeman and Miller (*Arch. Pediat.*, 1926, **43**, 421) overcame this difficulty by drying with sodium sulphate, but did not separate the fat from other ether-soluble substances, such as sterols. Numerous other methods have been proposed, but they are either subject to one of the above-mentioned inaccuracies or are unsuitable for the rapid treatment of a large number of samples.

We have adopted the following method:—The material was thoroughly mixed in a mortar, and 5 grms. were weighed into a 100-ml. beaker, to which 0·4 ml. of concentrated hydrochloric acid was added. The mixture was stirred to a homogeneous paste and allowed to stand for 5 minutes. When the dry-matter content was much above 25 per cent. a few drops of water were also added. Twenty-five grms. of anhydrous sodium sulphate were then added, and, after being well mixed, the mass was placed in a steam-oven for 15 minutes. The material was then powdered in a small mortar, transferred to an extraction thimble, and extracted for 4 hours with petroleum spirit A.R. (b.pt. 40° to 60° C.). After removal of the excess of solvent, the flask containing the extracted material was dried in the oven for 1 hour. Ten ml. of neutralised alcohol were added, the flask was gently warmed, and the fatty acid present was titrated with 0·05 *N* alcoholic sodium hydroxide solution, 5 ml. of a 1 per cent. solution of phenolphthalein being used as indicator. (We have found this large quantity advisable with the somewhat coloured solutions that are obtained.) One ml. of 0·05 *N* NaOH ≡ 0·0134 grm. of fatty acid, taking the average molecular weight of faecal fatty acids as 268 (Harrison, *Brit. J. Expt. Path.*, 1925, **6**, 139). This first titration gives the amount of fatty acid originally present either as such or in the form of soaps. A further 25-ml. quantity of the alcoholic sodium hydroxide solution was now added, and the mixture was heated on the water-bath under a reflux condenser, a blank determination being conducted at the same time. After one hour's brisk boiling the flasks were removed and the contents titrated with 0·05 *N* hydrochloric acid. From the difference between the results in the titrations the amount of fatty acid originally present as neutral fat was calculated by means of the factor given above.

Free fatty acid and soap may be differentiated by carrying out the process with a new sample, omitting the treatment with hydrochloric acid, so that only free fatty acids and neutral fat are extracted.

The combined sampling and experimental error was determined on a specimen of faeces by applying the above processes in six simultaneous determinations. The following figures were obtained, calculated on the undried material:—

	Fatty acids free and saponified Per cent.	Neutral fat as fatty acids Per cent.	Total fatty acids Per cent.
Sample 1..	2·32	0·79	3·11
,, 2..	2·38	0·60	2·98
,, 3..	2·43	0·77	3·20
,, 4..	2·50	0·77	3·27
,, 5..	2·27	0·83	3·10
,, 6..	2·39	0·79	3·18
Mean	2·382	0·758	3·140
S.D. of mean ..	±0·033	±0·033	±0·041
Percentage S.D. of mean	1·4	4·4	1·3
Mean of 30 analyses ..	2·284	1·134	3·418
Extremes	0·68–8·06	0·33–2·78	1·28–8·39

The last two lines in the above table refer to 30 analyses, selected at random, of specimens from various individuals on different treatments. It will be seen that the accuracy of the process is adequate for detecting differences likely to be encountered in work of this kind. The magnitude of the errors indicates that it is unnecessary to dry the specimen prior to mixing, in order to obtain a representative sample.

ERIC C. WOOD
T. W. SIMPSON

THE LABORATORY
VIROL LTD.
HANGER LANE, LONDON, W.5

Official Appointments

Dr. L. H. LAMPITT has been appointed a member of the Food Investigation Board of the Department of Scientific and Industrial Research.

THE Minister of Health has approved the following appointment:

FREDERICK WILLIAM EDWARDS as a Public Analyst for the Metropolitan Borough of Kensington from 1st January, 1935, in place of B. H. Gerrans, who is retiring on 31st December, 1934 (November 9th, 1934).

Notes from the Reports of Public Analysts

The Editor would be glad to receive the Annual or other Reports of Public Analysts containing matter of special interest to the Society. Notes made from such Reports would be submitted to the Publication Committee.

CITY AND COUNTY OF KINGSTON-UPON-HULL

Annual Report of the Public Analyst and Bacteriologist for the Year 1933

During the year reviewed, 10,410 samples and specimens were examined, of which 8245 were specimens for bacteriological examination. The total number of foods and drugs examined was 1835, of which 1594 were taken under the Food and Drugs (Adulteration) Act, 1928. Forty-nine of these were reported to be suspicious and 87 adulterated.

Flour in Curds.—Four of six samples submitted for analysis contained small quantities of wheat-flour; in one instance the amount was 4 per cent. of dry flour, and the sample was returned as of suspicious character. Such an addition of flour is unnecessary, but the practice appears to be growing, the makers stating that the use of flour assists in the separation of the curd in a satisfactory state of division. However, many makers do not add flour, which is undoubtedly an adulterant.

Dripping:—Twelve samples of dripping were examined, and 11 were found to be pure edible fats free from water and other extraneous matters, but one sample of pork dripping (adulterated) contained 25 per cent. of water together with salt and tissues, which left less than 75 per cent. of fat in the sample. An agreement entered into with the Master Butchers' Association some years ago requires such products to be marked and sold as "Pork Dripping with Gravy," and the vendor was cautioned.

Cocoa Tablets.—Two samples of a prepared mixture in tablet form, containing cocoa, dried milk and sugar, were not labelled in a satisfactory manner, there being no definite statement that foreign ingredients were present with the cocoa in the tablets. This make of tablets has been the subject of previous comment and warning, and it is possible that the samples represented old stock, as the label was unaltered. Further samples will be examined.

Potted Meat.—In 1933 the Hull City Council adopted the recommendations in my previous Report, that the amount of water in potted meat should not exceed 70 per cent., and that no food sold as potted meat or under a similar name, being loose potted meat, should be other than a pure meat product. The necessary steps were taken by the Town Clerk to inform traders of the standard required for these products.

During the year under review there were examined 31 samples of potted meat, 26 of which conformed to the above-mentioned standards; one was returned as of suspiciously poor quality (containing 76 per cent. water), being purchased before the new standards were set up, and four were adulterated, having an excessive water-content in one instance and in the remainder farinaceous additions, with or without excess of water.

Vinegars and Ultra-Violet Light.—The use of filtered ultra-violet light has been found helpful in differentiating in a number of cases between malt and artificial vinegars.

"Spearmint" Adulterated with Ailanthus.—A sample of mint, sold as "Spearmint" for medicinal purposes, contained about 16 per cent. of *Ailanthus* leaf. The vendor was prosecuted and fined £20. Ten of 16 samples of dried mint, not sold as a drug, also contained appreciable quantities of *Ailanthus* leaf, and in one case (wholesaler) a fine of £10 was imposed. A. R. Tankard

Ministry of Health

SALE OF FOOD AND DRUGS

EXTRACTS FROM THE ANNUAL REPORT FOR 1933–1934, AND ABSTRACT OF REPORTS OF PUBLIC ANALYSTS FOR THE YEAR 1933*

THE total number of samples analysed by Public Analysts during the year was 138,171, a slight increase over the number for the previous year (ANALYST, 1934, **59**, 110), and of these, 5·5 per cent. (4·6 per cent. in 1933) were reported as adulterated or not up to standard.

PRESERVATIVES.—In 138 cases food was found to contain prohibited preservatives, *e.g.* boron preservative in cream, sausages, meat pies, rennet and other articles; sulphur dioxide in sweets and in minced, potted, and other meat, desiccated soup, pepper, vinegar and table jelly; formaldehyde in milk; salicylic acid in lime juice and non-alcoholic wine; and benzoic acid in caviare. There was excess of permissible amounts of preservative in 81 cases, and in 160 samples the preservative would have been permissible if it had been declared on the label.

MILK.—Of 74,545 samples of milk examined, 5760 (7·7 per cent.) were reported against. "Appeal-to-cow" samples numbered 1068, and 380 were reported below the presumptive standard of the Sale of Milk Regulations, 1901. One sample was reported to be 23 per cent. deficient in fat and to be coloured with annatto, and added colouring matter was found in 8 other cases, whilst visible dirt was reported in 8 samples, formaldehyde in 6 samples, and 1·79 grains per gallon of sulphur dioxide in one sample. Twenty-four samples of graded milk were stated to be deficient in fat, and 20 skimmed milks were deficient in non-fatty solids, one being said to contain 79 per cent. added water.

CONDENSED AND DRIED MILK.—Twenty-four of 1171 samples of condensed milk were reported against; 16 contained the equivalent of less milk than stated on the label, 5 were deficient in milk solids, 2 were unfit for consumption, and 1 contained 125 parts per million of tin. Of 207 dried milks, 2 were deficient in fat, 3 should have been sold as skimmed milk, 1 was unlabelled, 1 contained the equivalent of less milk than indicated on the label, and 1 was not dried milk as defined by the Public Health (Dried Milk) Regulations.

CREAM.—Of 2171 samples of cream, 18 contained boron preservative, 11 were reconstituted or artificial cream, 9 were deficient in milk-solids, and 3 contained fat other than milk-fat. Three "rich" creams contained only 24 to 25 per cent. of fat, whereas fresh cream contains on an average about 50 per cent. of fat.

BUTTER AND MARGARINE.—Of 8903 samples of butter, 67 contained over 16 per cent. of water (in one case 36·5 per cent.), 3 had excess of free fatty acids; 12 consisted wholly or partly of margarine, and 1 contained boron preservative. Ten margarines (of 3180 examined) had excess of water, 2 contained more than 10 per cent. of milk fat, 1 (sold in error) was butter, and 3 were not properly labelled.

LARD AND OTHER FATS.—Only 3 of the 2688 samples examined were adversely reported upon, 1 for containing cotton-seed oil and 2 which consisted wholly of substitute fat. Thirty-three of 414 samples of shredded suet contained excess of starch. Two drippings (of 578) consisted entirely of hog fat, 4 contained excess of water or free fatty acids, and 1 was rancid.

CHEESE.—Of 1392 samples, 5 sold as "Cheshire Cheese" were deficient in fat (in 1 case to the extent of 53 per cent.), 6 wrapped in tinfoil contained excess of tin

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*** Obtainable at H.M. Stationery Office, Adastral House, Kingsway, W.C.2. Price 4d. net.**

(in 1 case amounting to 7·2 grains per lb.), and 3 sold as cream cheese were made from whole or separated milk.

BREAD AND FLOUR.—Four samples of bread (of 273 examined) were affected with "ropiness," and 1 contained powdered glass. Only 2 of the 1370 samples of flour examined were reported against, one for containing about 2 per cent. of soap flakes, and one for excess of sodium bicarbonate.

JAM AND MARMALADE.—The proportion of samples reported against (124 of 1773) is a considerable increase on any previous year. The majority were deficient in the fruit specified on the label or contained other fruit, 25 contained excess of preservative, and 5 were deficient in fruit and had also excess of preservative. One sample contained fungus in considerable amount.

VINEGAR.—Of 1746 samples, 98 were deficient in acetic acid, 34, described as malt or table vinegar, consisted wholly or partly of artificial vinegar, and 3 samples contained prohibited preservative.

SPIRITS AND BEER.—In 132 cases (of 1947) the spirit had been reduced to more than 35 degrees under proof. One beer (of 420 samples) contained phenolic disinfectant, one was a non-alcoholic imitation, and a third contained excess of preservative.

MISCELLANEOUS ARTICLES OF FOOD.—Over 31,000 samples of such foods as tea, coffee, cocoa, confectionery, sugar, dried fruit, pepper, mustard, cakes and biscuits, ice-cream, sausages, fish, rice, spices and condiments, and honey were examined. Eleven samples of tea were reported against; one was labelled "Digestive tea free from Tannin," but contained 12·7 per cent. of tannin, and a sample of liquid tea contained Glauber's salt. Twelve samples of coffee contained chicory; cocoa shell, foreign fat, sugar and arrowroot were present in cocoa. A sample of tinned spiced beef and tongue contained 190 p.p.m. of tin, a minced meat 3500 p.p.m. of boron preservative, and "savoury ducks" 425 p.p.m. of crystallised boric acid. Pollack, ling, haddock, cod or coal fish were all reported to have been sold as hake, megrim or witch as lemon sole, and lemon sole as Dover sole. Seventy-three samples of dried mint and 11 of mint sauce contained ailanthus leaf. A "concentrated lime juice" was a coloured and flavoured solution of citric acid and glycerin; barley and oatmeal were infested with acari, and the stocks were destroyed; seedless raisins were sold as sultanas, dried apricots as dried peaches, starch and other farinaceous matter foreign to arrowroot, as arrowroot; "macaroni with egg" contained no egg, and vitamins were absent from a "vitamin beverage." Arsenic was reported in yeast; copper in cider, dried pears, fruit drinks and canned beans; tin and lead in canned fish; lead in aerated water, coffee and curry powder, and tin in many samples of canned fruit and vegetables.

DRUGS.—Of 5328 samples examined, 270 (distributed over some 60 preparations) were reported against. Twenty-six samples of tincture of iodine were either deficient in potassium iodide or contained it in excess; 20 mercury ointments were deficient in mercury; 21 samples of Parrish's Food were deficient in phosphate of lime or iron; and 19 samples of sweet spirit of nitre were deficient in ethyl nitrite, in one case to the amount of 100 per cent. Sweet nitre balsam contained no balsamic principle; camphorated oil was deficient in camphor; syrup of figs contained salicylic or benzoic acid; Seidlitz powders had excess of tartaric acid, and saccharin was deficient in soluble saccharin to the extent of 95·6 per cent. Gregory's powder was made with oxide of magnesium, Glauber's salt was sold as Epsom salts, and sodium bicarbonate was supplied for carbonate of soda. A sample of "slimming tablets" consisted of a mixture of aperient drugs likely to cause chronic purging.

D. G. H.

Report of the Government Chemist upon the Work of the Laboratory*

FOR THE YEAR ENDING 31ST MARCH, 1934

THE usual chemical work for various Government Departments has been carried out (*cf.* ANALYST, 1933, **58**, 693), the total number of samples examined being 503,592—an increase of 42,597 on those of the previous year. The chief increases were in connection with the importation of hydrocarbon oils, the examination of beer, wine and spirits for duty under the Import Duties Act, 1932, samples of tobacco for exportation, and samples of British sugar, whilst there was a decrease in the number of imported samples examined for sugar. The duty of 1d. per gallon charged under the Hydrocarbon Oils Duty on oils other than light oils has involved the complicated examination of many articles in which hydrocarbon oil was one of the ingredients, and the quantity and character of the oil had to be determined. An increase of more than 8000 samples in connection with the Import Duties Act has meant a disproportionate increase of work, for much investigatory work is often necessary to determine the category of the substance being dealt with. The growing use of duty-free spirits and industrial methylated spirit is noted.

MINISTRY OF AGRICULTURE AND FISHERIES.—*Butter and Margarine.*—None of the 842 samples of butter, and only one of the 281 samples of margarine, contained over 16 per cent. of water.

Cheese.—In the 121 samples examined, the water varied from 31 to 59·2 per cent., and the fat from 20·5 to 64·8 per cent.

Cream.—Of 99 samples, one contained 67 per cent. of fat; three, 50 to 59 per cent.; and the remainder, 20 to 27 per cent.

Sheep Dips.—Four of the 78 samples examined were reported to be defective.

Fertilisers and Feeding Stuffs Acts, 1926.—Two fertilisers (a mixed fertiliser and a shoddy) and 11 feeding stuffs (meat meals, meat and bone meals, sharps, pig rations, laying meal and dairy nuts) were examined, 3 samples being from sellers. The results confirmed those of the agricultural analysts, except that, although 2 samples of sharps were found to contain the deleterious weed seeds alleged to be present, only traces of them were found. Castor-seed husk was not found in the portion of a sample of dairy nuts examined, and an excess, instead of a deficiency, in potash was found in a mixed fertiliser. This last sample had the appearance of a fine uniform powder, but contained large crystals of potash salts, which tended to separate from the remainder, and made satisfactory sampling very difficult. This was the probable explanation of the variations in the two sets of analytical results.

Agricultural Produce (*Grading and Marking*) *Act.*—Two hundred and thirty-five plain, 108 self-raising, and 175 Yeoman flours were tested; also, 25 samples of malt extract and extract-of-malt with cod-liver oil; 186 samples of cider, 131 of honey and 81 of Cheshire cheese—all under the respective Agricultural Produce Regulations. The miscellaneous products included wood-pulp board, dried eggs, dried diatoms, canned vegetables and butter.

CUSTOMS AND EXCISE.—The various Chemical Stations are now staffed by established officers on the staff of the Government Chemist, and the scope of the work has in certain cases been enlarged. There has been an increase of 8971 in the number of samples examined on that for the previous year.

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* Obtainable at H.M. Stationery Office, Adastral House, Kingsway, W.C.2. Price 9d. net.

Beer.—The total number of samples examined was 43,100—a slight increase on those of the previous year. The original gravity of wort was declared by the brewers at a figure between 1 and 3 degrees too low in 176 cases (of 4888). Nineteen samples of the 58 examined of non-alcoholic beer, herb beer and beer substitutes, contained from 2 to 8 per cent. of proof spirit. Arsenic was present in slight excess of the limit allowed (1/100th of a grain of arsenious oxide per lb. in solids or per gallon in liquids) in 25 of 2029 samples of beer and brewing materials.

Cocoa and Chocolate.—The number of samples examined rose to 10,174, much of the increase being from imported goods. About 800 samples of imported cocoa preparations and 600 of preparations (*e.g.* biscuits) containing sugar were analysed to determine the nature of the fatty ingredients and to assess their liability under the Ottawa Agreements Act.

Coffee and Chicory.—Of 1613 samples submitted (1087 for drawback), 26 of the imported samples were coffee substitutes composed of roasted cereals or roasted fig.

Hydrocarbon Oils Duty.—The total number of samples examined was 13,247, 5293 from imported and 7954 from exported goods, and of these, 10,001 were hydrocarbon oils and 3246 composite goods, such as enamels, paints, toilet preparations, etc. In 5 cases illegal mixtures of kerosene and motor spirit were found, and these were the subject of legal proceedings decided in favour of the Crown.

Import Duties Act, 1932, *Ottawa Agreements Act,* 1932. *Additional Import Duties Orders.*—The 12,916 samples examined included a wide range of articles, such as fabrics, leather, alloys, pigments, resins, pottery, paper, oils and fats, fertilisers, drugs, etc., and frequently involved difficult analyses.

Spirits.—Of the 13,339 samples of exported spirituous preparations examined, the declared strength had been overstated in 196. The number of imported samples was 10,567. Thirteen prosecutions were instituted for illicit distilling or other Revenue offences, and convictions were obtained.

Sugar, etc.—The number of samples in which sugar was determined was 70,852, compared with 74,414 in the previous year, and comprised a wide range of substances.

Tea.—Of 26,978 samples, 175 (representing 894 packages) were reported against, 88 on account of the presence of foreign substances and 87 as being unfit for human consumption.

Tobacco.—Of imported manufactured tobacco, 277 samples (272 of cigarettes) contained ingredients not allowed in tobacco in this country. The proportion of water was determined in 7396 samples of manufactured tobacco for home consumption, and the proportion of oil in 672 samples. The samples of manufactured tobacco and commercial snuff for export on drawback were 84,312—an increase of 16,885 on the previous year. Investigatory work of a scientific and technical nature has been found necessary during the year, and included the question of equalisation of temperature in electric ovens used for the determination of moisture (*cf.* ANALYST, 1934, 168).

MINISTRY OF HEALTH.—Thirty-five samples were found to contravene the Public Health (Preservatives, etc., in Food) Regulations; these comprised 31 samples containing sulphur dioxide, 3 containing benzoic acid, and one containing copper colouring matter, either contrary to the Regulations or in excess of the quantities allowed.

FOOD AND DRUGS ACT.—Twenty samples of food and one of medicine were examined during the year. The foods consisted of fifteen samples of milk alleged to be deficient in fat or non-fatty solids, or to contain formalin; 3 jams alleged to be deficient in fruit, 1 butter alleged to contain foreign fat, and 1 mint sauce alleged to contain foreign matter. The medicine contained an excess of quinine.

In 15 cases the results were in agreement, and in 5 cases in disagreement, with those put forward by the prosecution. The butter sample afforded no evidence of the presence of foreign fat. One sample of milk was not below the presumptive standard of the Sale of Milk Regulations. The proportion of fruit in 2 samples of jam was not inconsistent with the "full fruit standard," having regard to the natural variation in composition of the fruit, and no foreign matter was present in the mint sauce.

D. G. H.

Western Australia

ANNUAL REPORT OF THE CHEMICAL BRANCH MINES DEPARTMENT FOR THE YEAR 1933

THE Chemical Branch of the Mines Department, which is under the direction of the Government Mineralogist and Analyst (Dr. E. S. Simpson), is responsible for the analytical and investigational work required by the various Government Departments. It has been found necessary to "ration" to a slight extent the samples that may be submitted by the Departments, as well as by the general public. The total number of samples examined was 5678, and these were allocated to three sections: (i) Food and Drugs and Toxicology (755); (ii) Mineralogy (2864); (iii) Agriculture and Water Supply (2059). The following topics of interest, *inter alia*, are recorded:

BLEACHED TRIPE.—Two samples of tripe received from the Health Department were examined with reference to a complaint that, when cooked with onions, the tripe turned them green. The samples were somewhat disintegrated, strongly alkaline, and when macerated with water gave a p_H of 10, showing the presence of caustic soda and sodium carbonate. It was evident that the tripe had been treated in a bath of some strongly alkaline liquid which had been incompletely washed out, and the supplier confessed to the use of sodium peroxide. Tripe which had been so treated was reported as unfit for human consumption. Six samples of the liquor used by the wholesale supplier were examined with a view to ascertaining the bleaching agent used by him in tripe preparation. The solutions were all strongly alkaline, with the exception of one, which was evidently a wash-water. The analyses showed that the tripe was being treated in a bath of weak "sodium peroxide" solution with probably some sodium carbonate, with a view to bleaching and "plumping" it. In this treatment the fibres of the tripe become disintegrated and swollen, resulting in a condition known as "plumping." It is said that a considerable increase in weight takes place, 20 lbs. of tripe before treatment producing at least 25 lbs. after treatment. This process of bleaching may seriously affect the nutrient value of a foodstuff which is used chiefly by invalids, and the process should be prohibited. The use of hydrogen peroxide would be preferable, as no caustic alkali or sodium carbonate would be present in the resultant liquor, as is the case when sodium peroxide is used. Further investigations showed that fresh, untreated tripe was practically neutral, and slowly became acid, whilst the peroxide-bleached tripe was alkaline and became more so with lapse of time.

VINEGAR.—The manufacturers of five different brands of vinegar were prosecuted and convicted in the Perth Police Court for selling products that did not comply with the Regulations. The Foods Advisory Committee is considering the drastic amendment of the present vinegar regulations with a view to protecting the public from purchasing imitation vinegars that are placed on the market as genuine.

POISONING BY SODIUM FLUORIDE.—An unusual case of poisoning, in which a man took a spoonful of sodium fluoride in mistake for sodium bicarbonate, was investigated. Twenty-two grains of sodium fluoride were recovered from the stomach and its contents. The deceased had used the powder as the basis of a mixture to kill cockroaches, and had regarded it as identical with sodium bicarbonate. The Chief Inspector of Police was notified by letter that sodium fluoride should be placed on the list of scheduled poisons.

STANDARDS FOR COPPER CARBONATE FUNGICIDE.—The following standards were recommended for adoption by all the Australian States, and have been gazetted under the Plant Diseases Act, 1914, by Western Australia:

(*a*) It shall contain not less than 50 per cent. of copper (Cu) in the form of basic carbonate and/or basic sulphate or oxychloride; and the label upon the container in which the material or mixture is contained shall state, in addition to the percentage of copper, the form or forms of basic salt in which it occurs.

(*b*) It shall contain not more than one-quarter per cent. of copper in a form soluble in water.

(*c*) Not more than two-and-one-half per cent. of the material shall be retained on a standard I.M.M. 200-mesh sieve, when ten grms. of the material are shaken by hand for five minutes with 150 c.c. of water in a stoppered 500-c.c. Erlenmeyer flask and sieved in a gentle stream of water poured from the flask or a wash-bottle.

New Zealand

ANNUAL REPORT OF THE CHIEF CHEMIST, DEPARTMENT OF AGRICULTURE, FOR 1933–4

THE Annual Report of the Chief Chemist (Mr. B. C. Aston, F.I.C.) gives statistical details of the analyses of soils, fertilisers, etc., together with accounts of the investigation of special problems.

USE OF LIMONITE IN "BUSH SICKNESS."—Further investigation of the use of limonite (*cf.* ANALYST, 1934, 40) has shown that so-called "limonites" from different sources, or subjected to different degrees of heating or other conditions during preparation as a lick, may vary greatly in their feeding or curative value. A reduced solubility of the iron oxide was found to result from the substitution of a harder and denser deposit for a soft friable deposit, even when the ores were similar in chemical composition. Heating altered the solubility of various ores in different ways, but a temperature of from 500° C. to 600° C. was necessary before a considerable reduction of solubility could be shown by laboratory methods. When limited quantities of acid of about the same concentration as the gastric juice were used, the reduction of acidity occasioned by contaminating carbonate of lime reduced the amount of iron dissolved.

Lime, either as carbonate or slaked lime, used as a lick for ruminants, is so easily eaten in harmful amounts in "bush-sick" country that it is inadvisable to give this class of animals lime in this way. The use of lime carbonate as a top-dressing for pasture has proved so ineffective, or even harmful to ruminants in "bush-sick" country, that the liming of "bush-sick" pastures as a practice is strongly condemned. In places where the use of ineffective kiln-dried limonite had been responsible for serious loss of sheep, reversion to good air-dried limonite caused almost magical recovery of affected cattle. Limonite treatment, as a means of maintaining animal health and increasing production on "bush-sick" pumice country, is now generally regarded as standard farming practice, but the use of limonite as a top-dressing for pastures has been discountenanced as ineffective and wasteful. Owing to the uncertainty in the interpretation of the pasture analyses, due to the large amount of soil contamination in the majority of the samples, a special effort was made to secure samples relatively free from soil by means of enclosed plots in a few representative paddocks. Several samples much freer from contamination than any previously examined showed some interesting features. The iron was very low in most of the "sick" samples and somewhat higher in the healthy ones. Manganese was not reduced to a corresponding extent. The ratio of iron to manganese varied between 2 and 9 for the "sick" pastures (uncontaminated), averaging 4, whereas for the healthy pastures it varied between 1 and 2, averaging 1·4. As it seemed possible that the excess of manganese might be affecting the absorption or utilisation of the iron, further analyses of uncontaminated pastures and an experiment on feeding manganese to sheep on a moderately low iron diet are planned. Field experiments with limonite extending over two years have proved successful in raising a profitable crop of lambs where in previous years it was not found possible.

In connection with the investigation into the nature and prevention of eclampsia or grass staggers in dairy cows, it was suggested that dolomite, if finely ground, might prove a suitable source of magnesium for use as a lick. A supply of local material was obtained from Collingwood and has been passed on to the veterinary authorities for trial. An analysis of this material showed it to contain 40 per cent. of magnesium carbonate and 54 per cent. of calcium carbonate.

PAMPAS GRASS AS FODDER.—Preliminary analyses have shown that pampas grass contains from 30 to 40 per cent. of carbohydrates, calculated as dextrose, on the dry substance. The young leaves are exceptionally easy to browse, offering in this aspect a marked contrast to the mature toetoe grass (*Arundo conspicua*), the leaves of which at all stages of growth are fibrous and difficult to break off.

IODINE INVESTIGATION.—Sheep thyroids from 300 farms in the North Island and 500 farms in the South Island have been sampled and analysed, composite samples being prepared from each flock (*cf.* ANALYST, 1934, 188).

SOIL RICH IN IRON, ALUMINA AND TITANIA.—An especially interesting problem was presented by a type of soil derived directly from the underlying basalt found at Okaihau, North Auckland, and probably representative of a large area. It was stated that it had been found impossible to establish the usual grasses and clovers on this soil, and from a field inspection it appeared that the trouble might be connected with an excess of iron and alumina. A laboratory examination revealed a high percentage of iron and aluminium oxides, and a deficiency of available plant-food, especially phosphorus and calcium. The alkaline earths, potash, and phosphorus extracted by hydrochloric acid were also in low amounts. A fusion analysis gave the following composition expressed as percentages of air-dried soil: silica, 28·97; ferric oxide, 20·89; alumina, 20·83; titanium dioxide, 7·15; phosphoric acid, 0·11; calcium oxide, 0·21; magnesium oxide, 0·58; manganous oxide, 0·09; moisture, 2·67; loss on ignition, 18·54; total, 100·04. The percentage of titanium dioxide is remarkably high, and the ratio of silica to sesquioxides low. It seems, therefore, that this soil has some of the characteristics of a lateritic type. It is known that phosphorus is fixed in insoluble form by compounds of iron, aluminium, and titanium in the soil, so that application of phosphate to this soil would not be expected to give satisfactory results. It has been found, however, that silica in the form of colloidal silica or of kieselguhr has the effect of reducing the tendency of phosphorus to revert to insoluble forms, and the Okaihau soil suggested itself as a very suitable subject for experiment along these lines. It is remarkable that New Zealand danthonia grass grows readily in the scrub [largely *Leptospermum* (Manuka) and the naturalised *Hakea acicularis*] with which these lands are covered, being evidently able to exist, as do the Australian species of danthonia, under soil conditions which include very low phosphate-content. This suggested that these lands might be laid down in danthonia for small sheep-runs and gradually improved into mixed grazing farms.

WEED-KILLERS.—Weed-killer trials under difficult conditions were conducted with a large number of chemicals in an endeavour to find a cheaper, better, and less dangerous substitute for sodium chlorate. Approximately ninety tests, mostly under field conditions, were made with thirty-six different substances, including a large number of oxidising substances with properties somewhat similar to, but less dangerous than, sodium chlorate. Many of these were tried on ragwort at different strengths, either with diluent or fertiliser or in solution. Compared with sodium chlorate as a standard, the following were prominent among certain groups of substances potent in their action in killing ragwort: (1) hypochlorites of sodium and potassium; (2) chromates of sodium and potassium; (3) thiocyanates of ammonium, sodium, and potassium. Further experiments with these and other promising chemicals will be made if facilities and assistance are available.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs Analysis

Dithizon Test for the Detection of Heated Milk. K. Eble and H. Pfeiffer. (*Z. Unters. Lebensm.*, 1934, **68**, 307–310.)—Dithizon (diphenylthiocarbazone), which is extremely reactive towards oxidising agents, is applicable to the detection of peroxydase in milk, provided that the latter is rendered acid. The reagents required are: (i) 0·04 grm. of dithizon dissolved in 100 ml. of acetone; (ii) 20 per cent. lactic acid (or 75 per cent., sp.gr. 1·206 to 1·216); (iii) 1 per cent. hydrogen peroxide solution. Reagent (i) keeps well in a brown glass bottle.

In a stoppered glass cylinder, 10 ml. of the milk are shaken with 1 ml. of reagent (i) and then treated with either 1 ml. of 20 per cent. or 0·5 ml. of 75 per cent. lactic acid. After mixing, 1 drop (about 0·05 ml.) of reagent (iii) is added, and the whole is shaken vigorously for 10 to 15 seconds. The operations are carried out in diffused light, since strong light influences the colour. If a series of milks are to be tested, use may be made of a reagent prepared by dissolving 0·04 grm. of dithizon in 73 ml. of acetone, filtering, and adding 27 grms. of 75 per cent. lactic acid solution. Ten ml. of the milk are shaken with 1 ml. of this reagent, and 1 drop of 1 per cent. hydrogen peroxide is then added. This mixed reagent does not keep well.

Milk which has been pasteurised by sufficiently long heating at 85° C. gives a deep reddish-violet colour if 20 per cent. lactic acid is used, or a bluish-violet colour if 75 per cent. lactic acid is added. The colours persist unchanged for hours away from bright light. Raw milk gives at first a strawberry colour, which changes to beige or yellow after 2 minutes and to yellow after 3 minutes. Heated milk, to which 2 per cent. of raw milk has been added, gives, when 20 per cent. lactic acid solution is used, a violet-red colour, changing to brownish-red after 1 minute, to strawberry colour after 10 minutes, and to reddish-brown after

25 minutes; when 75 per cent. lactic acid is used, the successive colours are bluish-violet, grayish-violet, deep gray, and gray. With heated milk containing 10 per cent. of added raw milk, the colours are grayish-violet, strawberry, beige to yellow, and almost yellow (20 per cent. lactic acid), or grayish-violet, brownish, beige, and almost yellow (75 per cent. lactic acid). Thus the test is capable of indicating the presence of 2 to 3 per cent. of raw milk, and gives certain results with 5 per cent. or more.

T. H. P.

Dialysis of Milk: Factors Affecting the Distribution of Calcium and Phosphorus. L. H. Lampitt and J. H. Bushill. (*Biochem. J.*, 1934, **28**, 1305–1312.)—In order to obtain the "average" values, the authors used dried milk prepared from the morning and evening milkings of a herd at various seasons of the year. For the dialysis a collodion sac, containing 250 ml. of distilled water, was suspended in 900 ml. of milk for 2 days at 0°–5° C. The calcium was determined by ashing the dialysate in platinum, dissolving the ash in 0·5 *N* hydrochloric acid, washing the solution into a beaker and diluting it to 100 ml. Thymol blue solution was then added and more hydrochloric acid, if necessary, to give a pink colour. Then 5 ml. of 6·4 per cent. oxalic acid solution were added and the whole was heated to boiling. Ammonia solution (*N*) was added, drop by drop, with stirring, until the solution was definitely yellow ($p_H = 3$). After being heated on a water-bath for 3 hours the solution was cooled, and the precipitate was collected on a No. 41 Whatman filter-paper and washed with a solution prepared as follows:—five ml. of 6·4 per cent. oxalic acid solution were diluted to 100 ml. and then adjusted by the addition of ammonia solution to p_H 3·0. The filter-paper and washed precipitate were ashed in a platinum dish by heating with a Bunsen burner, followed by an hour at 1,000° C. in a gas muffle. The lime so produced was dissolved in 5 ml. of 0·5 *N* hydrochloric acid, washed into a conical flask with cold, boiled water and titrated with 0·5 *N* sodium hydroxide solution, methyl red being used as indicator. The total and inorganic phosphorus were determined by the method already described by the authors (*Biochem. J.*, 1933, **27**, 711). Titratable acidity and p_H were also determined.

The authors find that dilution of milk causes a decrease in acidity and an increase in dialysable calcium and inorganic phosphorus. An increase in acidity by bacterial action also increases the amount of dialysable calcium and inorganic phosphorus. It has been found impossible to compare results with those obtained by other workers, as these gave no indication of acidity control or of the amount of acidity present. Acidity and dilution do not appear to affect the dialysable organic phosphorus present. The calcium in spray-dried milk is affected less by dilution than that in pasteurised milk. This may be due to heat or to dehydration, but the application of direct heat has much less effect. By the use of the "static" method of dialysis under controlled conditions the results for an "average" milk were as follows:

Dialysable calcium	25–33	per cent. of the total amount in the milk.
,, phosphorus, total ..	43–51	,, ,, ,, ,, ,, ,, ,, ,, ,,
,, ,, inorganic	33–41	,, ,, ,, ,, ,, ,, ,, ,, ,,

S. G. S.

Jaffé-Folin Reaction of Hydrolysed Gelatin. H. Mohler and E. Helberg. (*Z. Unters. Lebensm.*, 1934, **68**, 254–270.)—The effect of gelatin added to soup-cubes (*cf.* ANALYST, 1934, 180) on the Jaffé–Folin reaction for creatinine (with picric acid and sodium hydroxide solution) has been studied both by observation of the colour-formation and spectrophotometrically. After treatment with hydrochloric acid, gelatin may be confused with creatinine as determined in this way. Of the hydrolytic products yielded by the gelatin, glycine (or diketopiperazine) and histidine cause the initial appearance of the colour in this reaction, arginine and histidine tending to intensify the coloration. T. H. P.

Bitter Glucoside of the Olive. W. V. Cruess and C. L. Alsberg. (*J. Amer. Chem. Soc.*, 1934, **56**, 2115–2117.)—A bitter principle was obtained by boiling olives with water, separating the oil, concentrating the aqueous portion, mixing it with acetone, filtering, evaporating the filtrate almost to dryness, usually *in vacuo*, taking up the residue with absolute acetone, and again evaporating almost to dryness. This treatment was repeated several times, the acetone solution being allowed to stand for some days to allow mannitol to separate. Finally, the residue was taken up with water, the solution was neutralised with barium hydroxide and filtered, and sufficient ammonium sulphate was added to "salt out" the bitter principle, which was further purified by fractional precipitation with lead acetate at approximately p_H 4·5. Then followed decomposition with hydrogen sulphide, evaporation to dryness, solution in absolute acetone, solution in water, electrodialysis, solution in acetone, and precipitation with diethyl ether, these operations being repeated several times. As thus obtained, the bitter principle was amorphous, and had specific rotation − 145° to −148° in 0·5 to 3 per cent. aqueous solutions. It was found to be a bitter glucoside readily hydrolysed by an enzyme occurring in olive leaves, by "Pectinol" (a commercial *Penicillium* mould preparation), and slowly by emulsin. Invertase did not attack it. On acid hydrolysis *d*-glucose and an ether-soluble bitter ester were liberated, and on hydrolysis by "Pectinol" the rotation became dextro-rotatory. A crystalline acid, isolated from the products of alkaline hydrolysis, gave the same qualitative reactions and had the same m.pt. and X-ray spectrum as caffeic acid. An unidentified crystalline phenol (not pyrocatechol) was also isolated. The bitter principle appears to have both a glucoside and an ester linkage. The glucoside was present in the olive flesh to the extent of about 1 per cent., but its concentration was considerably higher in green fruit of the Mission and Manzanillo varieties and much lower in the Ascolano and Sevillano varieties. D. G. H.

Colobot Peel Oil. (*Perf. and Ess. Oil Rec.*, 1934, **25**, 269–270.)—An essential oil is obtained from the peel of the Philippine citrus fruit "colobot" [*Citrus hystrix*, D.C. var. *torosa* (Blanco), Webster]. The large green mature fruits yielded more essential oil than the smaller younger fruits, and the odour (resembling that of limes) was also finer. The spiny colobot tree, found wild in Batangas province, is also cultivated to some extent, and grows to a height of about 6 metres. The smaller fruits are 3·5 to 4 cm. in transverse diameter, and the larger 5 to 5·5 cm. The yield of oil is high (2·15 per cent.), and a sample had the following values:—sp.gr. at 30°/4° C., 0·8506, $[\alpha]_D^{30}$ + 25·69, n_D^{30}, 1·4665; saponification value, 11·4; and acid value, 0·93. Distillation of 100 ml. yielded the following fractions:—Below 160° C., 2·0 ml.; 160–166° C., 4·5 ml.; 166°–170° C., 19·0 ml.; 170°–172° C., 23·5 ml.; 172°–175°, 12·0 ml.; 175°–180°, 16·0 ml.; and residue, 21·0 ml. The oil contains double-bond compounds, and gives very pronounced reactions for aldehydes. When treated with a saturated solution of sodium bisulphite, crystals of a bisulphite addition product were formed, and these, when decomposed, gave a positive reaction for citronellal, 26 per cent. of which was found in the original oil (Baker and Smith's method). The unaltered portion, which had a pine-like odour, appeared to consist of a mixture of terpenes. It is suggested that the oil would be a useful constituent for perfumes. D. G. H.

Coffee-bean Oil. H. A. Schuette, M. A. Cowley and C. H. Chang. (*J. Amer. Chem. Soc.*, 1934, **56**, 2085–2086.)—Green Santos coffee beans were washed with tetrachloroethane to remove the wax, of which approximately 0·24 per cent. was obtained. The oil (2·7 per cent.) was then extracted with petroleum spirit; it was greenish-brown and yielded 5 per cent. of a pungent volatile substance on steam-distillation. The fatty oil had the following characteristics:—sp.gr. at 25/25° C., 0·9653; n_D^{25}, 1·4790; saponification value, 195·5; iodine value (Wijs), 100·7; Reichert–Meissl value, 0·36; Polenske value, 0·4; acid value, 7·05; unsaponifiable matter, 12·63 per cent. (with iodine value, 153·8); hydroxyl number, 22·82; saturated acids, 33·60 per cent.; unsaturated acids, 38·02 per cent. (with thiocyanogen value, 91·57); iodine value of total fatty acids, 94·11; and of the unsaturated acids, 153·61. The exclusion of the wax from the oil has caused the values to differ from those previously recorded for coffee-bean oil, the iodine value, refractive index and sp.gr. being considerably higher. The oil was found to contain the following fatty acids; oleic, 12·36; linolic, 25·66; myristic, 2·19; palmitic, 20·17; stearic, 9·13; and arachidic, 2·11 per cent.

D. G. H.

Fatty Oil from Pumpkin Seed. Constitution of Linolic Acid. J. L. Riebsomer and G. A. Nesty. (*J. Amer. Chem. Soc.*, 1934, **56**, 1784–1785.)—The pumpkin seed contained 9·6 per cent. of moisture and 36·6 per cent. of an ether-extractable oil with the following characteristics:—sp.gr. at 20/4° C., 0·9159; n_D^{20}, 1·4737; saponification value, 174·2; iodine value (Hanus), 116·8; Reichert–Meissl value, 1·5; acetyl value, 2·76; acid value, 12·49; unsaponifiable matter, 1·58 per cent.; mean molecular equivalent of saturated acids, 269·0 (with iodine value 9·6); molecular equiv. of unsaturated acids, 289·2 (with iodine value 138·2); saturated fatty acids (calculated on the oil) corrected, 11·4, unsaturated fatty acids, 76·3 per cent. The unsaturated acids were separated by the lead salt and ether method, and the methyl esters were prepared. The unsaturated acids were also brominated, and the linolic acid was determined. No hexabromide was produced. The methyl esters were treated with ozone, and the resulting products were fractionally distilled *in vacuo* at 24 mm. The first fraction (b.pt. 54° to 58° C.) contained caproic acid, whilst pelargonic acid was found in fraction 3 (b.pt. 103°—106° C.) and azelaic acid in fraction 5 (b.pt. 123°–175° C.). From the results the formula for linolic acid was deduced to be

$$CH_3\text{-}(CH_2)_4\text{-}CH{=}CH\text{-}CH_2\text{-}CH{=}CH\text{-}(CH_2)_7\text{-}COOH.$$

The saturated acids were found to consist of palmitic and stearic acids in the proportions of 6·2 and 5·2 per cent., respectively, in the oil, whilst unsaturated fatty acids consisted of 35·9 per cent. of oleic acid and 40·4 per cent. of linolic acid (calculated on the oil). D. G. H.

Highly Unsaturated Fatty Acids in the Oils of some Common Fowls and in Animal Fats. J. B. Brown and C. C. Sheldon. (*J. Amer. Chem. Soc.*, 1934, **56**, 2149–2151.)—The methyl esters of the fatty acids from 5 samples of goose oil, 4 of chicken oil, 2 of duck and one of turkey oil, were fractionated, also those from the fats of a lamb, a calf, an ox, and a reindeer, and the fats were also examined by the usual methods (bromination, etc.) for the presence of small amounts of highly unsaturated acids. The presence of linolenic acid was definitely indicated in 2 specimens of goose oil, and was probably present in another goose oil and in turkey oil. In eight other specimens of avian oils amounts varying from 0·21 to 1·16 per cent. of highly unsaturated acids, mostly arachidonic acid, were found, and the four animal fats contained traces of similar acids other than arachidonic acid. It seems probable that small amounts of highly unsaturated fatty acids occur generally in animal fats. D. G. H.

Highly Unsaturated Acids in Herring, Cod-liver, Pilot Whale Blubber, and Aburazame Liver Oils. Y. Toyama and T. Tsuchiya. (*J. Soc. Chem. Ind. Japan*, 1934, **37**, 530–534B.)—Herring oil was subjected to methanolysis in the presence of potassium hydroxide, and the methyl esters were distilled up to 240° C. (10 mm.). The residue from the distillation was saponified, and after separation of unsaponifiable matter, the fatty acids were liberated and treated by the sodium salt and acetone method. The sodium salts soluble in acetone were separated, acidified and converted into methyl esters, which were distilled up to 215° C. (at 2 mm.). The fatty acids liberated from the final (saponified) residue consisted mainly of highly unsaturated C_{24} acids and their polymerised products; they were fractionally precipitated from their solution in acetone as the sodium salts, and the fatty acids separated from the fraction of highest unsaturation were dissolved in ether and brominated. The ether-insoluble bromides were separated and debrominated, yielding a highly unsaturated acid, $C_{24}H_{36}O_2$, which was called *nisinic acid*. This nisinic acid (or its isomer), which has also been found in cod-liver oil, pilot whale, blubber oil, and aburazame (*Squalus sucklii*) liver oil, had the following analytical values:—sp.gr. at 15/4° C., 1·5131 to 1·5137; iodine value, 402·0 to 416·0; neutralisation value, 154·9 to 158·9. On hydrogenation nisinic acid yielded impure *n*-tetracosanic acid. D. G. H.

New Eicosenoic Acid in Pilot Whale Oil. Y. Toyama and T. Ishikawa. (*J. Soc. Chem. Ind. Japan*, 1934, **37**, 536–537B.)—The methyl esters from the body oil of the pilot whale were fractionated, and the fatty acids from the fraction boiling at 215 to 222° C. (10 mm.) were converted into lithium salts and treated with 50 per cent. alcohol. The fatty acids from the insoluble portion were treated with lead acetate in 95 per cent. alcohol, the insoluble lead salts were filtered off, the fatty acids from the lead salts in the filtrate (iodine value 102·2, neutralisation value, 179·7) were again converted into methyl esters and fractionated, and the fatty acids from the fraction boiling at 215 to 222° C. were repeatedly recrystallised from 80 per cent. alcohol at $-10°$ C. The final product, which was in the form of fine needles, had iodine value 80·5, neutralisation value 180·2, and m.pt. 23·5 to 24° C. The m.pt. of the acid was lowered to about 18° C. by admixture with pure gadoleic acid (m.pt. 24 to 24·5° C.) from cod-liver oil. The product of oxidation by Hazura's method, after recrystallisation from 90 per cent. alcohol, had neutralisation value 162·1 and m.pt. 126·5° to 127° C., and its m.pt. was lowered to about 113° C. by a mixture with dihydroxy-arachidic acid obtained by the oxidation of gadoleic acid. The conclusion was drawn that the eicosenoic acid obtained is an isomer of gadoleic acid, and it is proposed to term it *gondoic acid*. The hydrogenated product, after recrystallisation from 95 per cent. alcohol, had m.pt. 74° to 74·5° C., and this was not lowered by admixture of the product with arachidic acid prepared from erucic acid by fusion with potassium hydroxide. It is assumed, therefore, that gondoic acid has no branched chain, and that it is a monoethylenic acid. D. G. H.

Gadoleic Acid in Sei Whale and Humpback Whale Oils. Y. Toyama and T. Ishikawa. (*J. Soc. Chem. Ind. Japan*, 1934, **37**, 534–436B.)—Gadoleic acid, $CH_3(CH_2)_9CH{=}CH(CH_2)_7COOH$, has been found previously in cod-liver oil and in Japanese sardine oil, herring oil, and sukeso dara (*Theragra chalcogramma*) liver oil. The sei whale and humpback whale oils used had the following characteristics, respectively:—sp.gr. at 15/4° C., 0·9248, 0·9212; n_D^{20}, 1·4748, 1·4732; saponification value, 186·9, 187·8; iodine value (Wijs), 129·8, 115·4; unsaponifiable matter, 1·84, 1·08 per cent.; acid value, 2·5, 1·85. The oils were subjected to methanolysis, and the methyl esters were separated and roughly fractionated. The fatty acids from the fractions distilling at 210° to 225° or 230° C., were separated and converted into the lithium salts, and the portion insoluble in 50 per cent. alcohol was decomposed with hydrochloric acid. The fatty acids were dissolved in 95 per cent. alcohol, the solution was treated with lead acetate, the precipitated salts were filtered off, and the fatty acids from the filtrate were converted into the methyl esters, which were then repeatedly fractionated. The fatty acids from the fractions boiling at 217° to 218° C. (sei whale) and 215° to 220° C. (humpback whale oil) were isolated and purified until comparatively pure gadoleic acid was obtained (sp.gr. at 25°/4° C., 0·8868, n_D^{25}, 1·4597; m.pt., 24–24·5° C.; neutralisation value, 179·8; iodine value, 80·5). D. G. H.

Iodimetric Determination of Morphine. Laurence and Labarre. (*J. Pharm. Chim.*, 1934, **20**, 353–358.)—The process described depends on the formation of the insoluble morphine tri-iodide, $C_{17}H_{19}O_3NI_3$. This is readily hydrolysed by water, with liberation of the iodine, but, under the conditions given, the method yields results agreeing with those of the B.P. method and requires far less material and time. With opium powder, 0·5 grm. is mixed with about 2 grms. of slaked lime and 10 ml. of water in a mortar. After 15 minutes, the mixture is transferred to a filter and washed with water to give 50 ml. of total filtrate. Ten ml. of this are neutralised in a conical flask with 3 to 5 drops of glacial acetic acid, 2·5 grms. of potassium iodide and exactly 10 ml. of 0·1 *N* iodine solution being then added. If necessary, precipitation of the tri-iodide is aided by rubbing with a glass rod. The mixture is shaken repeatedly during three minutes, and is afterwards poured on to a funnel with a porous glass base and filtered by gentle suction. The filter is washed with a few ml. of water, and the unused iodine is determined by titrating the filtrate with 0·04 *N* thiosulphate solution. Each ml. of 0·04 *N* iodine used for the precipitation represents 0·0038 grm. of anhydrous morphine or 0·00505 grm. of morphine sulphate.

With tincture of opium, 2 ml. are evaporated on the water-bath to a soft extract, which is mixed with about 1 grm. of calcium hydroxide by means of a glass rod. The pasty mass is diluted with 5 ml. of water and, after 15 minutes, is brought on to a filter. The residue is washed with two portions of water to extract the morphine from the lime, 20 ml. of filtrate being collected. Ten ml. of the liquid (≡ 1 ml. of the tincture) are neutralised with 3 to 5 drops of glacial acetic acid and titrated as above.

With morphine tablets or pills, 5 to 10 of these are pounded in a mortar. The subsequent procedure is that described for opium powder.

Any codeine extracted with the morphine does not interfere with the determination, its concentration being too low. Other alkaloids are eliminated by the lime. T. H. P.

Analytical Chemistry of Pentamethylene-tetrazol (Cardiazol). J. J. L. Zwikker. (*Pharm. Weekblad.*, 1934, 71, 1170–1182.)—Cardiazol, $C_6H_{10}N_4$, m.pt. 57° to 58° C., is very soluble in water (to give a neutral solution) and in most organic solvents; it is very volatile, and, when warmed, it emits an odour resembling that of benzaldehyde. It is separated (*e.g.* from organs) by extraction with acidified alcohol, the extract being evaporated at a low temperature and the residue extracted with pure chloroform. It may be further purified by precipitation from a solution in water with mercuric chloride, which has been crystallised from alcohol, when the crystalline compound $C_6H_{10}N_4$, $HgCl_2$ (solubility 1 : 800, m.pt. 175° C.) is formed; alternatively, or in addition, it may be "salted out" from its aqueous solution by addition of ammonium sulphate, and then removed by extraction with chloroform. The ordinary reagents for alkaloids are unsatisfactory as tests (*e.g.* Mayer's reagent and picric acid give negative results), but cardiazol forms insoluble crystalline salts very readily, and these may be identified microscopically. A solution of chromic acid in ether gives a brown precipitate, and if 1 mgrm. of cardiazol in 5 ml. of water containing 1 drop of hydrochloric acid is shaken with potassium dichromate, hydrogen peroxide and chloroform, a blue perchromate (which is visible in the chloroform layer) is formed. A solution of ferrocyanide or ferricyanide of potassium in hydrochloric acid precipitates needles or prisms, and a pale pink colour results on oxidation with warm potassium permanganate in the presence of sulphuric acid. The reagent prepared by dissolving 1 grm. of ammonium molybdate in a mixture of 10 ml. of water and 2 ml. of 4 *N* hydrochloric acid, and then diluting to 20 ml. (*cf.* van Giffen, *id.*, 1932, 69, 1479) is sensitive to 1 : 1000, but reacts with substances (*e.g.* quinine and ephedrine) which are frequently associated with cardiazol. The mercuric chloride reaction (*supra*) is sensitive to 1 : 5000, and precipitates thin hexagonal plates, and the cyanide and iodide behave similarly, although in the last case the reaction should be carried out with acetone or alcohol as the solvent. A 20 per cent. solution of cadmium iodide precipitates $C_6H_{10}N_4,CdI_2,H_2O$ as very insoluble needles from 1:5000 solutions of cardiazol in water, and the reaction is assisted by the presence of ammonium sulphate, but inhibited by potassium iodide. Similarly, cadmium chloride forms $C_6H_{10}N_4,CdCl_2,3H_2O$, and a mixture of cadmium sulphate and potassium thiocyanate produces droplets which, after warming, form trapezium-shaped crystals. In general, the thiocyanates of the heavy metals give poor results, although the mercuric and cupric salts give crystals (analogous to the cadmium salts) and blue droplets, respectively. The best reagent is prepared by warming a solution of 200 mgrms. of cupric chloride in a few drops of water with a solution of 250 mgrms. of sodium sulphite in 5 ml. of water; 2 ml. of 4 *N* hydrochloric acid are added to the cool solution, and the mixture is diluted to 10 ml. If 2·5 ml. of this reagent are added to 10 ml. of the solution of cardiazol, doubly-refracting needles of $C_6H_{10}N_4,2CuCl_2$ are obtained (sensitiveness 1:40,000). Quinine and related alkaloids, ephedrine, morphine, atropine, novocaine, pilocarpine, antipyrine and pyramidon do not react, and urotropine gives crystals which are not doubly-refracting and are easily distinguished. This reaction may also be used as a means of recovering cardiazol quantitatively. J. G.

Identification of Superol (Quinosol). G. H. Wagenaar. (*Pharm. Weekblad*, 1934, **71**, 1122–1124.)—Superol (*o*-hydroxyquinoline sulphate, or quinosol) is used as an antiseptic (*e.g.* in gargles, sera and vaccines), or as a preservative (*cf.* Coppens, *id.*, 1930, **67**, 1321). It gives with ferric chloride, an emerald-green colour, which is stable in the presence of alcohol or acetic acid, this reaction being characteristic of the *o*-hydroxyquinoline group, and it is precipitated by the usual general reagents for alkaloids; barium chloride reacts normally with the sulphate group. Picric acid precipitates small fine hair-like needles which form radiating tufts (sensitiveness, 1:5000), and solid potassium ferrocyanide produces aggregates of dark brown lozenge- and plate-shaped crystals (1:300). Platinic chloride, mercuric chloride, sodium carbonate, sodium bicarbonate, ammonia and sodium hydroxide all precipitate characteristic needle-shaped crystals which, in most cases, are long and radiate from common centres; with sodium hydroxide, however, an excess of reagent redissolves these. With silver nitrate the precipitate is similar in structure to calcium sulphate, but more strongly anisotropic. The principal crystal-forms are illustrated. J. G.

Biochemical

Fate of Dulcitol and Dulcitan in the Animal Body. C. J. Carr and J. C. Krantz. (*J. Biol. Chem.*, 1934, **107**, 371–376.)—Feeding experiments showed that the removal of one molecule of water from dulcitol, to form the anhydride dulcitan, destroys the capacity of the former compound to be stored as glycogen in the liver of white rats. Each substance tends to reduce tissue glycogen storage. Neither compound affects the respiratory quotient of white rats, and neither is effective in relieving insulin shock. When either compound was administered orally, no significant rise in the blood sugar of rabbits was observed. S. G. S.

Thiolacetic Acid as a Reagent for the Determination of the Inorganic Iron-Content of Biological Materials. S. L. Tompsett. (*Biochem. J.*, 1934, **28**, 1536–1543.)—The thiolacetic acid method for the determination of iron has been applied to the hen's egg, human urine and human blood. The iron in the hen's egg and blood may be determined by adding the thiolacetic acid to the material, then a little trichloroacetic acid, filtering, and using the filtrate for the colorimetric determination. Urine requires treatment with nitric acid, followed by sulphuric acid and perchloric acid. The hen's egg contains about 1·25 mgrm. of iron, all of which is in the inorganic form, human serum about 0·20 mgrm. of iron per 100 ml., and human whole blood about 1·3 mgrm. of iron per 100 ml. Normal human urine contains less than 0·01 mgrm. of iron per litre, but this may rise to over 2·0 mgrms. per litre in nephritis. S. G. S.

Determination of Cystine. Use of the Zeiss Photometer. J. H. Bushill, L. H. Lampitt and L. C. Baker. (*Biochem. J.*, 1934, **28**, 1293–1304.)—The use of the Zeiss photometer has been applied to the colorimetric determination of cystine by the method introduced by Sullivan (*U.S. Pub. Health Reports*, No. 1084, 1926), which employs quinone, sodium sulphite and sodium hydrosulphite as reagents. The criticism of this method put forward by Rimington (private communication, 1929) and Lugg (*Biochem. J.*, 1933, **27**, 668) has been confirmed by photometric measurements. It has been found that the best results are obtained when light of wave-length 530mμ is used. The colour is affected by oxygen, and the use of the Sullivan technique may involve an error of ± 25 per cent., although this can be reduced to ± 8 per cent. by the Lugg technique. The modified Lugg technique enables cystine in pure solution to be determined within ± 5 per cent., but since an occasional error of ± 15 per cent. is encountered, it is believed that other unknown factors affect the result. In the presence of protein, such as hydrolysed caseinogen, the limit of error is ± 8 per cent. Since cysteine in pure solution may be determined with a limit of error of ± 4 per cent., it is thought that the reduction of cystine to cysteine introduces another factor into the determination of the former substance. S. G. S.

Colorimetric Method for the Determination of Fructose in Blood and Urine. J. H. Roe. (*J. Biol. Chem.*, 1934, **107**, 15–22.)—The method, which is an elaboration of that published by Kronenberger and Radt (*Biochem. Z.*, **190**, **161**) in 1927, depends on a colour reaction between de-proteinised material and resorcinol in the presence of hydrochloric acid. One part of blood is added to seven parts of distilled water and allowed to stand for a few minutes in order that haemolysis may take place. One part of a 10 per cent. solution of hydrated zinc sulphate and one part of a 0·5 *N* solution of sodium hydroxide are added and the solution is filtered. Two ml. of the filtrate are placed in a test tube, and in each of three similar test tubes 2 ml. of standard fructose solution are placed, the standards used containing 0·1, 0·05, and 0·025 mgrm. of fructose per ml. To each tube 2 ml. of a 0·1 per cent. solution of resorcinol in alcohol (95 per cent.) and 6 ml. of a mixture of 1 vol. of water with 5 vols. of concentrated hydrochloric acid are added. The solutions are mixed by shaking the tubes, which are then maintained at 80° C. for 8 minutes, after which they are removed to a beaker and cooled in running water, and the solutions are compared in a colorimeter. In the examination of urine, 2 ml. are placed in a small Erlenmeyer flask, and 18 ml. of a 1 per cent. solution of acetic acid are added. To this 0·2 grm. of acid-washed activated charcoal is added, and the whole is well shaken and allowed to stand for 5 minutes with occasional shaking. The solution is filtered, and 2 ml. of the filtrate are placed in a test-tube, three tubes containing standard solutions of fructose being also prepared. The standards should be made by diluting a stock solution with 1 per cent. acetic acid, so that the acetic acid concentration may be the same throughout. The procedure is then the same as for blood. Any protein in the urine may be removed by the same method as that used for the blood analysis. S. G. S.

Volumetric Determination of Inositol. L. Young. (*Biochem. J.*, 1934, **28,** 1428–1434.)—The method of Fleury and Marque (*J. Pharm. Chim.*, 1929, **10**, 241) for the determination of polyhydric alcohols and related substances by the use of potassium iodomercurate in alkaline solution has been modified to give results of increased accuracy. Into a dry 100-ml. pyrex conical flask are pipetted 5 ml. of the solution to be determined, containing not more than 5 mgrms. of inositol. Next, 3 ml. of the potassium iodomercurate reagent are introduced, followed by 4 ml. of 30 per cent. sodium hydroxide solution. Lastly, 2 ml. of well-shaken barium sulphate suspension (20 grms. of barium sulphate, "X-ray," in 80 ml. of water) are added, and the contents of the flask are mixed by gentle rotation. The flask is then placed in a boiling water-bath with the level of the water of the bath well above the level of the contents of the flask. As the reaction proceeds a red precipitate forms first and is soon replaced by a gray-black precipitate of mercury. After 45 minutes' heating the flask is removed and clamped in a bath of running water. It is essential that no agitation of the contents of the flask take place from the time the heating begins until the iodine is added. The flask is then cooled for 5 minutes, and 8 ml. of 20 per cent. sulphuric acid are added without moving the flask. After 5 minutes more in the cooling bath, the flask is removed and 5 ml. of 0·1 *N* iodine solution are measured into it. By carefully rotating the flask at intervals during a period of 10 minutes the mercury is readily brought into solution. Any undissolved mercury can be seen as a gray-black precipitate collected at the centre of the bottom when the flask is viewed from underneath immediately after being rotated. At the end of the 10 minutes the excess of iodine is titrated with 0·02 *N* sodium thiosulphate solution, fresh starch solution being used as an indicator. It is necessary to prepare a graph indicating the relationship between mgrms. of inositol and ml. of 0·02 *N* sodium thiosulphate solutions. A graph of this nature, which is linear, is included in the original paper. The potassium iodomercurate solution is prepared by dissolving 288 grms. of potassium iodide in water and adding this, with shaking, to a solution of 108 grms. of mercuric chloride. The mixed solutions are diluted to one litre and filtered if necessary.

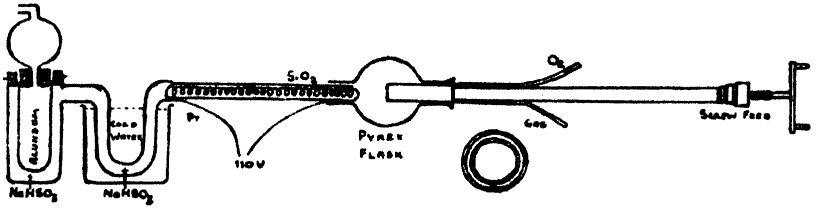
If glucose and inositol are present together, the glucose may be removed by fermentation. Fresh baker's yeast is suspended in five times its weight of water and centrifuged. Portions of the filtered supernatant liquid are examined by the iodomercurate method from time to time. After about four washings a constant value of about 0·1 mgrm. of inositol per grm. of yeast is obtained, and the yeast is then suspended in four times its weight of water and the solution is used for fermenting the glucose. In a 30-ml. pyrex beaker are placed 10 ml. of the solution to be fermented, and the beaker is covered with a watch glass and incubated at 37° C. for a short time. Then 100 ml. of the yeast suspension at room temperature are added, and the whole is incubated at 28° C. The mixture is stirred at intervals with a glass rod left in the beaker, and after the necessary period the yeast is filtered off on a sintered glass filter (Schott and Gen., Jena, 1G4). The beaker is rinsed with three approximately equal portions of water, making 10 ml. in all, and the rinsings are passed through the filter. The filtrate is evaporated to dryness, the residue re-dissolved in water, the solution evaporated again, and the final residue dissolved in water; its inositol-content is then determined. S. G. S.

Determination of Inositol in Animal Tissues. L. Young. (*Biochem. J.*, 1934, **28**, 1435–1443.)—The finely-minced tissue is extracted in a closed conical flask with its own weight of acetone. After 24 hours' extraction, with occasional shaking, the liquid is poured off through a glass-wool plug in a filter-funnel. The plug is washed with a few ml. of 70 per cent. acetone and transferred to the flask. After another 20 hours' extraction the liquid is separated and the tissue residue pressed on a small press. It is then moistened with 70 per cent. acetone and pressed again. All the acetone extracts and expressed liquids are combined and filtered on a Buchner funnel. The acetone is removed by distillation on a gently-heated water-bath, and the residual aqueous extract is evaporated to about 100 ml., filtered, and extracted twice with equal volumes of ether, a few drops of alcohol being added if an emulsion forms. The combined ethereal extracts are extracted with half their volume of water, and the aqueous layer is added to the aqueous extract from the acetone. This solution is heated gently to remove the ether, evaporated, filtered, and made up to 100 ml. in a volumetric flask. This aqueous extract is now poured into a dry pyrex litre conical flask, the 100-ml. flask is rinsed with two successive 5 ml. of water, and these in turn are allowed to drain into the litre flask. From a burette are then added slowly, with shaking, 30 ml. of acid mercuric sulphate solution [27 grms. of mercuric sulphate in 100 ml. of 10 per cent. (by weight) of sulphuric acid at 5° C., any precipitate forming at room temperature being filtered off.] Solid barium carbonate (160–170 grms. A.R.) is then added to neutralise the mixture. The flask is rotated until most of the carbon dioxide has escaped. It is then stoppered and shaken vigorously, care being taken to release the pressure at intervals. When no more pressure develops, the mixture is tested with litmus paper, and, if necessary, more barium carbonate is added until the mixture does not turn blue litmus red. It is then filtered on a dry Buchner funnel into a dry flask under reduced pressure, and a carefully measured amount (75–95 ml.) of the filtrate (which should be water-clear and colourless) is transferred to a 125-ml. beaker. This is heated on a water-bath, the liquid is made just acid with two or three drops of concentrated sulphuric acid, and a steady stream of hydrogen sulphide is bubbled through it for one minute. The solution is now filtered into a 250-ml. conical flask, the precipitate is well washed with hot water, and the hydrogen sulphide is expelled by boiling the filtrate on a sand-bath for a short time (addition of a piece of porous pot may be necessary). The solution in the conical flask is then transferred to a 100-ml. beaker and concentrated on a water-bath to 10 ml. To this hot solution 3 grms. of crushed crystalline barium hydroxide are added, the liquid is heated on a water-bath for 5 minutes, with occasional stirring, and 40 ml. of ethyl alcohol are added slowly, with vigorous stirring. At one point in the process the contents of the beaker appear to solidify. The precipitate is allowed to settle at room temperature for 2 to 3 hours and then filtered under reduced pressure on a sintered glass filter (Schott and Gen., Jena, 3G3). The beaker is rinsed twice with 5 ml. of absolute alcohol, and the washings are passed through the filter. The precipitate is then transferred by means of a small spatula to the original 100-ml. beaker. The small residue on the filter is dissolved in hot water and added to the main precipitate (volume 40 to 50 ml.). The beaker is heated on the water-bath, a slight excess of hot 2 *N* sulphuric acid solution is added, and heating is continued for 45 to 60 minutes. The barium sulphate is filtered off and washed with hot water until the volume of the filtrate (contained in a 150-ml. beaker) is about 125 ml. This solution is then concentrated to about 3 ml., transferred to a 50-ml. pyrex conical flask, and carefully concentrated on an electrically heated sand-bath to 3 ml. When the flask is cool 30 ml. of acetone and 15 ml. of ether are added, the sides of the flask are scratched with a glass rod to induce crystallisation, and the flask is firmly stoppered and placed in an ice-chest for 24 to 36 hours. The precipitate which forms is filtered under reduced pressure on a sintered glass micro-filter (Schott and Gen., Jena, 12G3) and washed with acetone and ether. The conical flask and micro-filter are dried at 100–110° C. for a short time, and the material on the filter and that adhering to the flask are dissolved in water, and the solution is filtered, if necessary, and made up to a known volume. Inositol in this solution is then determined by the method described in the previous abstract. The amount of inositol in the sample of tissue taken is obtained by multiplying the quantity found in the final solution by the factor obtained by dividing 140 by the volume of filtrate taken after the acid mercuric sulphate precipitation. S. G. S.

New Method for the Determination of Iodine [in Blood and Organic Substances]. D. R. McCullagh. (*J. Biol. Chem.*, 1934, **107**, 35–44.)—The method was worked out for blood samples, but can be applied to any organic material. Ten ml. of blood (or equivalent amounts of other substances) are placed, together with 12 ml. of a saturated solution of potassium hydroxide in a 300-ml. nickel crucible, and heated gently over a Bunsen flame. Care is necessary at this stage, as foaming may occur. When foaming abates, the material on the sides of the crucible is washed down with water, the boiling is continued for a few minutes, and the sides of the crucible are again washed several times with water. Finally, the mixture is boiled until the foaming ceases. The crucible is then heated for about 30 minutes in a muffle-furnace at 250° C. until the volatile and inflammable gases have been expelled. The temperature is then increased to 360° C. for 10 minutes, after which the crucible is removed and cooled. Water, in sufficient quantity to dissolve all the easily-soluble matter, is now added to the crucible, the lumps being broken with a glass rod. Any excess of water is boiled off gently until a paste is formed on cooling and stirring. If 25 ml. of 95 per cent. ethyl alcohol are now added, the paste forms a fluid sludge which separates at the bottom of the crucible. Any material adhering to the sides of the crucible can be scraped down into the fluid sludge with the stirring rod. After the mass has been stirred for several minutes the alcohol is decanted into a 300-ml. nickel crucible containing 1 ml. of a saturated solution of potassium hydroxide. The sludge is leached four more times with 10-ml. portions of alcohol. The alcohol, which contains all the iodine, is evaporated on a steam-bath and the contents of the crucible are dried gently over a flame. The crucible is then placed in a muffle-furnace at 385° C. for 10 minutes, a stream of oxygen (2 litres per minute) being passed through the furnace during ashing. The cooled residue in the crucible is dissolved in water, and the solution is filtered into a 500-ml. Claissen flask. The side-tube of this fits into the upper end of a Liebig condenser, the lower end of which dips under the surface of a mixture of 25 ml. of water, 0·5 ml. of 3 per cent. sulphuric acid, and 0·5 ml. of 10 per cent. sodium bisulphite solution contained in a 250-ml. Fresenius absorption flask. To the Claissen flask are now introduced 10 ml. of 50 per cent. sulphuric acid, 2 ml. of 10 per cent. ferric sulphate solution and 2 ml. of 30 per cent. hydrogen peroxide solution. The presence or absence of ferric hydroxide acts as indicator, and, if necessary, more acid may be added to make the solution strongly acid. The liquid, the total volume of which should be about 250 ml., is distilled for half an hour with frequent additions of 30 per cent. hydrogen peroxide solution, until the volume in the Claissen flask is about 50 ml. Distillation must be brisk. The distillate is then transferred to a 600-ml. beaker, and carbon dioxide and sulphur dioxide are expelled by boiling for 3 minutes. Immediately afterwards 10 per cent. potassium hydroxide solution is added until the solution is alkaline to litmus (not more than 1 ml. should be necessary). The alkaline solution is boiled, evaporated to about 10 ml., and transferred to a 50-ml. Erlenmeyer flask by washing the beaker three times with small quantities of iodine-free water. One drop of methyl orange solution is added, and the solution is neutralised with 3 per cent. sulphuric acid, two drops being added in excess. One drop of bromine is now added, and the solution, when shaken, should turn yellow. It is then evaporated to about 2 ml. and cooled on ice. One drop of 1 per cent. starch solution and a minute crystal of potassium iodide are added, and the solution is titrated with a 0·001 *N* solution of sodium thiosulphate, using a microburette. Each ml. of 0·001 *N* thiosulphate solution equals 21·2 micrograms of iodine.

S. G. S.

Iodine-Content of Potatoes. J. F. McClendon, E. Barrett and T. Canniff. (*Biochem. J.*, 1934, 28, 1209–1211.)—Potatoes were washed free from soil, dried in a current of air, ground in a coffee-mill, and dried again in an oven at 100° C. Samples weighing from 50 to 200 grms. of dried material were ashed by two methods. One was by using an electric furnace at 400° C. for 36 hours, removing the sample when redness appeared, allowing it to smoulder, and replacing it when smouldering ceased. The other method was to use a combustion tube (depicted in the diagram), as follows: The dried sample was powdered, packed in a Visking sausage-casing and placed in the screw feed, the open end of which was surrounded by an annular opening through which the oxygen was emitted to burn the sample. The ash from either method of ashing was ground in a 200-ml. ball-mill with three portions (50 ml. each) of 85 per cent. alcohol, which was evaporated, the residue being transferred to a boat and heated in a simple combustion tube to which was attached a small wash-bottle containing sodium bisulphite solution, and this solution, together with the washings of the tubes, was added to the ash, which was rubbed with a glass rod. To this extract was added 1 mgrm. of sodium azide, the whole being then acidified with phosphoric acid, evaporated to 10 ml., transferred to a separating funnel, and extracted twice with 1 ml. of carbon tetrachloride. The carbon tetrachloride extracts were compared in a micro-colorimeter with a standard solution containing 0·1 mgrm. of iodine per ml. The method of ashing in the electric furnace gave low results; but the loss was constant, so that an analyst knowing the loss his technique gave, could use this method for comparing the iodine-contents of potatoes from various districts without having recourse to the combustion-tube method. The authors find that potatoes have a very low iodine-content (85 to 400γ per kilo.). S. G. S.



Origin of Vitamin *D* in Cod-Liver Oil: Vitamin *D* Content of Zooplankton. A. M. Copping. (*Biochem. J.*, 1934, **28**, 1516–1520.)—Mixed zooplankton, from the coarse and medium mesh silk plankton nets, consisting mainly of small crustacea (copepods, with *Pseudocalanus elongatus* Boeck predominating, was submitted to various tests, in order to ascertain if any vitamin *D* was present. The McCollum line-test indicated that some antirachitic activity was present, but the test was not really satisfactory. Prophylactic experiments with a low-phosphorus rachitogenic diet showed, in the copepod material, a degree of antirachitic activity which was considerably greater than could be accounted for by its phosphorus-content. It is, therefore, concluded that these copepods contain sufficient vitamin *D* to make this constituent of the zooplankton a good source of the factor in the food of cod. S. G. S.

Bacteriological

Accidental Presence of Acrolein in Cider and Perry Spirits: Its Formation at the Expense of the Glycerol. G. Warcollier, A. Le Moal and J. Tavernier. (*Ann. Falsif.*, 1934, **27**, 430–432.)—Acrolein in a spirit may be detected by its rapid action on Nessler's solution, with formation of a black precipitate of metallic mercury (*cf.* ANALYST, 1932, **57**, 387, 578). The acrolein is produced by a bacillus 0·75μ in width, and varying in length from 2 to 8μ according to its age. This organism grows slowly on glucose-haricot broth-gelatin or glucose-yeast water-gelatin, either as a stab or a plate culture, forming white spherical colonies of pin-head size after 15 days. The bacillus is at first highly motile and occurs both as curved and as obtuse-angled, broken rods. It retains its activity over long periods, a culture sealed up for three years growing rapidly in a suitable medium. It may be obtained as a pure culture by: (1) growing it in yeast water-glucose, centrifuging, and transferring the deposit to yeast water-glycerol of p_H 6·5, or (2) seeding it directly into yeast water-glycerol of p_H about 8, the acidity increasing during growth to p_H 6.

To prevent the formation of acrolein in cider and perry, the fruit should be thoroughly washed to remove adherent soil, the worts well defecated, and the plant completely sterilised. T. H. P.

Toxicological

Gas Warfare and Foods. W. Plücker. (*Z. Unters. Lebensm.*, 1934, **68**, 313–320.)—The properties required in substances to be used in chemical warfare are discussed and the pertinent physical constants are given for the materials thus used during the European war. In considering the effects of these on foodstuffs, distinction is drawn between foods rich in water, such as meat, milk, beer, or wine, those poor in water, like grain, flour, shell-fruits, coffee, cheese, fats, etc., and those preserved in metallic or glass containers.

Phosgene and "perstoff" (ethyl perchloroformate) are strongly absorbed by wet foods, with immediate decomposition into hydrogen chloride and carbon dioxide. Meat thus contaminated may be rendered edible by washing it with very dilute sodium carbonate solution, which may perhaps also remove arsenious acid or stannic acid derived from arsenic trichloride or stannic chloride mixed with the phosgene. With other foods, except cheese and fats (for which the mode of action of the gas is unknown), treatment with a current of warm, dry air is suggested. Containers need only washing with sodium carbonate solution and then with water. Phosgene or perstoff in air may be detected by passing some litres of the air through potassium iodide-starch solution, iodine being liberated. Also, phosgene gives a blue colour with a solution of benzidine in hydrochloric acid, and, when passed through cold-saturated aniline water, it forms diphenylurea of m.pt. 235° C. Phosgene may be determined by weighing the diphenylurea (dried at 70° C.) or by passing the air through a known amount of water and titrating the hydrochloric acid formed.

Chloropicrin has irritant properties similar to those of phosgene, but causes also severe vomiting. Since the war it has been used to combat plant pests, rats, mice, lice, etc. It does not affect the baking quality of grain or flour, although the germinating capacity of grain is lowered. From dry foods it is removable by intense aeration, but it is questionable whether it can be eliminated from foods rich in water so as to render them edible. It acts on potassium iodide in methyl alcoholic solution, giving carbon tetra-iodide, potassium chloride, and potassium nitrite, and may be determined by means of either of these potassium salts.

Dichlorodiethyl sulphide (mustard gas, yellow cross, yperite) may be removed from foods low in water-content in the same way as phosgene, but no means is yet known of treating contaminated wet foods. It may be detected in air by means of either sodium-platinum iodide paper, which turns first purple and then blue, or sodium sulphide solution, from which it precipitates pure diethylene sulphide, m.pt. 111–112° C. Titration of the chlorine formed with silver solution serves for its determination.

Diphenylchloroarsine and diphenylcyanoarsine (blue cross) may be removed from foods in the same way as chloropicrin. To detect them in air, 10 to 15 litres of the air are passed through a 10-cm. layer of cotton-wool, which is afterwards extracted repeatedly with alcohol. The extract is evaporated on a water-bath to 10 or 20 ml., which is mixed with an equal volume of water; a layer of benzene is then superimposed and titration with 0·001 *N* iodine solution is carried out as described by Sieverts (*Z. angew. Chem.*, 1922, **35**, 17): 1 ml. of the iodine solution ≡ 12·7 mgrms. of the blue cross. Chloroacetophenone, methyldichloroarsine, diphenylaminochloroarsine, and diphenylaminocyanoarsine are also considered, but few experimental data for them are available.

As regards the identification of the gas used, phosgene appears in the dead body never as such, but always as hydrogen chloride; if the air breathed contained phosgene in low proportion, hydrogen chloride may not be detectable in the body. Mustard gas decomposes into dithioglycol and hydrogen chloride, but is detectable by its smell. If this is excluded, any free hydrogen chloride found in the clothes may be regarded as a decomposition product of phosgene. Nitrous acid or nitrogen iodides are often detectable by their smell and indicate the use of such substances as ammonium nitrate, picric acid and trinitrobenzene. Fresh meat which has been in contact with only small amounts of nitrous gases is edible, and with larger amounts washing with dilute sodium carbonate solution suffices to remove the contamination. From food products poor in water, nitrous gases may be expelled by aeration or, possibly, by washing with very dilute sodium carbonate solution. Peat and kieselguhr act as energetic absorbents for the toxic substances dealt with above, and are recommended as a protection for grain in bags. T. H. P.

Agricultural

Selenium Injury to Wheat Plants and its Inhibition by Sulphur. A. M. Hurd-Karrer. (*J. Agric. Res.*, 1934, **49**, 343–357.)—Selenium is absorbed by plants from soils containing it and is injurious in relatively small amounts. It is present in the soil of certain areas where the vegetation is toxic to animals, causing a disease now suspected to be due to selenium. It has also been found in plants growing along drainage canals from seleniferous springs, and may be present in a soil through inadvertent addition as an impurity in superphosphate and ammonium sulphate, and where fungicides or insecticides containing it have been used. It has been suspected that plant injury by selenium might be due to its replacing sulphur in some organic compound, or it may replace sulphur in the metabolism of sulphur bacteria, and possibly in plant metabolism (*Amer. J. Botany*, 1925, **12**, 82); this hypothesis receives support from the fact that adsorbed selenium has been found in intimate association with the protein in wheat (*Science*, 1933, 78, 124). The present paper deals with the relation between the concentration of available sulphur in the substratum and the degree of injury produced in wheat by sodium selenate. Sub-lethal concentration of sodium selenate (15 to about 30 p.p.m. in the clay loam used) produced a snow-white chlorosis, often accompanied in sand cultures by a pink colour. With older plants only the leaves emerging subsequently show the chlorosis, although the old leaves may turn yellow if the concentration is high enough. There is a progressive diminution of chlorosis on successive leaves as the plants become older. The presence of sulphur has a marked influence on the toxicity of the selenate; in water cultures a concentration of 0·1 p.p.m. of sodium selenate produced distinct injury in a few weeks when sulphur was absent, but if 192 p.p.m. of sulphur were present, 18 p.p.m. of the selenium salt was required to have a similar effect. No visible injury resulted where the proportion of selenium to sulphur was 1 : 12 or less, the point of minimum detectable injury being between 1 : 9 and 1 : 11; if the proportion was 1 : 8 or higher, chlorosis was apparent, and at 1 : 2 growth was almost completely stopped. Injury from selenium to plants growing in a greenhouse may be inhibited by the addition of sulphur in elementary form or as sulphate, the amount required varying with the toxicity of the selenate in the particular soil.

D. G. H.

Organic Analysis

Determination of Thallium in its Organic Compounds. S. S. Nametkin and N. Melnikow. (*Z. anal. Chem.*, 1934, 98, 414–416.)—The substance (0·1 to 0·5 grm.) is heated with 10 to 15 ml. of strong sulphuric acid on the water-bath, with gradual addition of 1 to 3 grms. of powdered permanganate. After 10 minutes' heating, 120 ml. of water are added and the excess of oxidant is removed with oxalic acid or hydrogen peroxide (if the latter, the excess is destroyed by boiling). The colourless solution is treated with bromine-water until a faint yellow tint persists; the free bromine is eliminated by adding a few drops of a 5 per cent. aqueous solution of phenol. Potassium iodide (0·5 to 1 grm.) is added, and the liberated iodine is titrated with 0·01 to 0·02 *N* thiosulphate, with starch as indicator.

W. R. S.

Determination of Basic Dyes by Precipitation with Phosphotungstic Acid. R. W. Payne. (*J. Soc. Dyers and Col.*, 1934, **50**, 320.)—Fifty ml. of a boiling 3 per cent. solution of phosphotungstic acid are added to a boiling solution of 0·1 grm. of dye in 1 per cent. hydrochloric acid, and boiling is continued for a few minutes. The precipitate is allowed to settle and is then filtered off in a Gooch crucible and washed with hot water until free from chlorides; it is dried at 120° C. until constant in weight, and, after ignition, the residue of $P_4(W_2O_7)_{12}$ is weighed. The mean values obtained for the factors for the dye-base (*i.e.* parts of dye-base to 1 part of ash) were:—Methylene blue, 0·233; diamond fuchsine (S.C.I.), 0·169; malachite green (L.B.H.), 0·216; chrysoidine-R, 0·242; rosaniline hydrochloride, 0·146; auramine hydrochloride, 0·184. Solutions of auramine should not be heated above 60° C., and for methylene blue the concentration of acid should be doubled.

J. G.

Variable Action of Acids on Hide Substance and a New Method of Detecting Harmful Acids in Leather. G. Otto. (*J. Amer. Leather Chem. Assoc.*, 1934, **29**, 290–311.)—An extract of the leather in water is made (*cf.* E. Müller and A. Luber, *Collegium*, 1933, 401) by digesting 1 grm. of pieces, 0·5 mm. thick, with 50 ml. of doubly-distilled water for 1 hour in a porcelain vessel (to avoid contamination by alkali from glass). Quinhydrone is then added to the decanted liquor (0·05 grm. per 10 ml.), and, after 30 minutes, 10 ml. are transferred to the titration-vessel, the bottom of which ends in a narrow glass tube provided with an ungreased stopcock up which a solution of potassium chloride is drawn before adding the sample, so that a small quantity is left just above the cock. This increases the conductivity of the cell without affecting the results. The remainder of the apparatus and procedure are those normally employed, 0·01 N sodium hydroxide solution being added from a micro-burette, 0·15 ml. at a time, with rapid stirring. Potentiometric curves are given for a number of leathers treated with various tanning agents, and an attempt is made to judge the amounts of strong acids and buffers present (and thence the permanency of the leather on storage) from the slope of the curves between p_H 4·0 and 5·5, expressed as the tangent of the angle (ϕ) between this part of the curve and the ordinate. Leathers tanned with sulphited or non-sulphited quebracho yield only small amounts of buffering substances; chestnut tans have the reverse effect. Leathers treated with strong acids are distinguishable from those processed with weak acids and, under the author's conditions of working, if tan ϕ is 0·75 or less, traces of damaging acids are present. The combination between acids and hide substances has also been investigated, and it is possible, after saturation of the hide with the acid, to remove hydrochloric and sulphuric acids completely by hydrolysis, although weak acids (*e.g.* from sulphonic acid tans and from substantive dyestuffs) are less easily removed. Such non-hydrolysable acids can, in general, displace the hydrolysable acids from combination with the hide-substance. If hide substance is completely saturated with a sulphonic acid tan, it loses its amphoteric character and has the p_H value 3·0. J. G.

Inorganic Analysis

Organic Reagents in Qualitative Analysis. II. Analysis of the Common Metals of the Ammonium Sulphide Group. L. Lehrman, H. Weisberg and E. A. Kabat. (*J. Amer. Chem. Soc.*, 1934, **56**, 1836–1838.)—A scheme is put forward by which it is possible to detect 1 mgrm. of any one of the metals in this group (iron, aluminium, chromium, nickel, cobalt, zinc, manganese) in the presence of 500 mgrms. of the others, alone or in combination. The sulphides, obtained in the course of the group separation, are dissolved in 12 ml. of *aqua regia*; the solution is evaporated to 1 ml. and diluted to 20 ml., and any sulphur is filtered off. Iron is precipitated with cupferron solution, and to the filtrate 5 ml. of 3 N nitric acid are added. The solution is boiled for 2 minutes, cooled, and diluted to 50 ml.; 3 grms. of sodium acetate are added, hydrogen sulphide is passed through the solution until no further precipitation occurs, and the precipitate is filtered off (giving filtrate *A*). The precipitate is treated with 25 ml. of boiling 1·5 *N* hydrochloric acid; the solution obtained is evaporated to 10 ml., cooled, and filtered if necessary, any residue being rejected. The solution is made slightly alkaline with ammonia, and nickel is precipitated by the addition of a saturated acetone solution of dimethylglyoxime. The precipitate is removed by filtration, and the filtrate, which is coloured brown if cobalt is present, is evaporated to 5 ml., cooled, filtered if necessary, acidified with acetic acid, and an equal volume of a 5 per cent. solution of 8-hydroxyquinoline in 2 *N* acetic acid is added; the formation of a yellow precipitate indicates zinc. Filtrate *A* (above) is evaporated almost to dryness after the addition of 15 ml. of 3 *N* nitric acid; the residue is boiled for 3 minutes with 20 ml. of hexamethylene-tetramine solution (10 per cent.) and filtered (giving filtrate *B*). The precipitate, containing the hydroxides of chromium and aluminium, is dissolved in 20 ml. of hot 2 *N* hydrochloric acid. One half of this solution is cooled, and an equal volume of 8-hydroxyquinoline solution in 2 *N* acetic acid is added: the formation of a yellow precipitate indicates aluminium. To the other half of the solution are added 5 ml. of 3 *N* nitric acid, 5 ml. of *N*/4 silver nitrate and 1 to 3 grms. of ammonium persulphate; the solution is evaporated to 5 ml., cooled, filtered if necessary, and tested for chromium with either hydrogen peroxide or diphenylcarbazide. Filtrate *B* is made alkaline with sodium hydroxide, 1 to 2 grms. of sodium peroxide are added, and the liquid is heated to boiling and filtered. The precipitate is washed with water, and, to test for the presence of manganese, is dissolved in nitric acid and oxidised to permanganate with sodium bismuthate. S. G. C.

Volumetric Method for Lead. I. Tananaeff. (*Z. anal. Chem.*, 1934, **99**, 18–21.)—The method is based upon the precipitation of lead chlorofluoride, PbFCl. The precipitant contains 8·400 grms. of sodium fluoride and 11·692 grms. of sodium chloride per 100 ml., and the chlorine-content must be accurately determined. For the determination of lead in bearing-metal, 0·5 to 1·5 grm. is dissolved in strong nitric acid, and the liquid is diluted and filtered into a 100-ml. flask. The filtrate is neutralised to methyl orange with strong sodium hydroxide solution, treated with a known excess of precipitant, and made up to volume. The excess of chlorine is titrated in 25 to 50 ml. of the filtrate with silver nitrate solution after addition of a few drops of fluorescein and starch solutions (Fajans, ANALYST, 1923, **48**, 401). The error is stated to be 0·2 to 0·4 per cent.; the quantity of lead in the solution should be at least 0·1 grm. Only silver and mercurous salts interfere. W. R. S.

Quantitative Precipitation of Copper by Tannin. M. B. Darbinian and A. G. Kankanian. (*Z. anal. Chem.*, 1934, **99**, 29–32.)—Copper is quantitatively precipitated by tannin from acetate solution; the precipitate is chestnut-brown. The warm solution is treated with about 1 grm. of ammonium acetate, and drop by drop with 25 ml. of 2 per cent. tannin solution, and left for a few minutes on the water-bath. The precipitate is collected, washed with hot water, ignited, and dissolved in nitric acid, and the copper is determined iodimetrically. The precipitation is not quantitative from ammoniacal solution, the precipitate being more or less soluble according to the ammonia concentration. W. R. S.

Precipitation of Cobalt and Palladium by Nitro-β-Naphthol. C. Mayr. (*Z. anal. Chem.*, 1934, **98**, 402–408.)—The reagent is a one per cent. solution of α-nitro-β-naphthol in 50 per cent. acetic acid. *Cobalt.*—For the determination of cobalt in steel, a solution of the metal, containing about 0·02 grm. of cobalt, is evaporated to remove acid, and the iron is precipitated with a minimum of zinc oxide emulsion. The liquid is adjusted to 500 ml., and an aliquot portion of the filtrate is evaporated with 1 ml. of hydrochloric acid to a bulk of 5 to 10 ml. The solution is treated with 10 drops of hydrogen peroxide and with sodium hydroxide, and the resulting black precipitate is dissolved in 70 ml. of glacial acetic acid. The liquid is diluted with 120 ml. of hot water, treated with 30 ml. of reagent, and heated to boiling. The precipitate is allowed to settle, collected in a porous crucible, washed three times with 30 per cent. acetic acid, and then with hot water, and dried at 130° C. to constant weight; composition, $(C_{10}H_6ONO_2)_3Co$; cobalt factor, 0·09463. *Palladium.*—The solution should not contain more than 5 per cent. of acetic acid. The precipitation is carried out as above, the precipitate being washed first with 5 per cent. acetic acid, then with water Composition $(C_{10}H_6ONO_2)_2Pd$; palladium factor, 0·2210. W. R. S.

Volumetric Determination of Potassium with Methylene Blue following its Precipitation as Potassium Picrate. A. Bolliger. (*J. Biol. Chem.*, 1934, **107**, 229–234.)—The method of determining potassium previously described (*Proc. Roy. Soc., New South Wales*, **1933**, **67**, 240) has been extended. For the precipitation, the material should not contain more than twice as much sodium as potassium, which should be present as chloride or perchlorate. Ammonium salts must be removed, but calcium and magnesium do not interfere. The sample is dissolved in a minimum amount of warm water and, if it consists mainly of potassium salts, about ten volumes of a 25 per cent. solution of alcoholic calcium picrate are added. After being mixed the solution is allowed to stand in a covered vessel for 2 hours at room temperature. If nearly as much sodium as potassium, or more, is present, 20 to 30 volumes of calcium picrate solution should be used and the mixture allowed to stand overnight at room temperature in a stoppered bottle. If the sodium-content is low, the precipitate is washed repeatedly with 4 volumes of ether containing 4 per cent. of ethyl alcohol until a washing with pure ether is colourless after being in contact with the precipitate for 10 minutes. If the precipitate contains much sodium picrate, the ethereal wash-liquid will remain yellow and the sodium picrate must be extracted with ethyl alcohol saturated at room temperature with potassium picrate. This is accomplished by shaking the precipitate with the wash-alcohol and leaving the liquid in contact with the precipitate for half an hour. The precipitation and washing may be done in a centrifuge tube and the solution centrifuged, the supernatant liquid being decanted; or, they may be done in flasks and the filtration carried out on a sintered glass funnel. After sufficient washing the precipitate is dissolved in hot water, and either the whole or aliquot portions (up to 3 mgrms. of potassium) of the solution are transferred to a separating funnel containing chloroform. This solution is then titrated with 0·001 *N* methylene blue solution. The end-point is reached when the aqueous-layer is colourless; after the addition of excess of methylene blue solution, it should remain permanently blue. The calcium picrate solution is prepared by boiling together 24 grms. of picric acid, 10 grms. of calcium carbonate and 100 ml. of water until the evolution of carbon dioxide ceases. The solution is filtered and evaporated to dryness. The residue is dissolved in absolute alcohol, and the solution is diluted to 100 ml. and filtered. S. G. S.

Volumetric Determination of Fluorine in Fluorspar. I. Tananaeff. (*Z. anal. Chem.*, 1934, 99, 21–26.)—This rapid method is based on the conversion of the fluorine into lead chlorofluoride (*cf.* abstract on p. 845). The finely-powdered mineral (0·5 grm.) is fused with 3 grms. of sodium potassium carbonate in a platinum crucible until the fused mass is perfectly clear. The crucible is cooled in water, and the melt is disintegrated in water with the aid of a spatula. The liquid is transferred to a 500-ml. conical flask, diluted to 300 ml., and treated with an excess of nitric acid and 10 ml. of sodium silicate solution (10 grms. SiO_2 per litre). After being heated for a short time the solution, which should be quite clear, is treated with 25 ml. of *N* sodium chloride, and the same volume of approximately *N* lead nitrate, solution. The hot solution is neutralised to methyl orange with strong sodium hydroxide solution, fresh indicator being added when necessary. The white precipitate (PbFCl) does not interfere. The solution is transferred to a 500-ml. flask, cooled, and made up to volume, and, after standing for some minutes, is filtered through a large dry paper. Two hundred ml. of filtrate are titrated with 0·5*M* silver solution after addition of a few drops of fluorescein and a little starch solution. The results thus obtained ranged from 99·40 to 100·25 per cent. when applied to pure fluorspar. A determination can be completed in about one hour. W. R. S.

Rapid Determination of Sulphate with the Use of a Collecting Agent. J. E. Orlow. (*Z. anal. Chem.*, 1934, 98, 326–329.)—The gravimetric determination of small amounts of sulphate in water, etc., is often delayed by the finely-divided state of the precipitate of barium sulphate, which does not settle well. The author adds a measured volume of dilute aluminium chloride solution of known strength (3 to 10 mgrms. of Al_2O_3) to the boiling solution, and then barium chloride, and neutralises with ammonia, with methyl red as indicator. The weight of the alumina is subtracted from that of the ignited precipitate. W. R. S.

[*Abstractor's Note.*—Filter-paper pulp acts as a collector in the acid solution.]

Titration of Chloride and Bromide with Mercurous Nitrate with Bromphenol Blue as Adsorption Indicator. I. M. Kolthoff and W. D. Larson. (*J. Amer. Chem. Soc.*, 1934, 56, 1881–1884.)—Chloride and bromide in concentration greater than 0·04 *N* and 0·01 *N* respectively can be titrated with 0·1 *N* mercurous nitrate solution, 6 drops of bromphenol blue solution (1 per cent. of the sodium salt in water) being used as indicator. In neutral solution the colour change is from yellow to lilac, and is reversible; it is sharp to within 1 drop of titrating solution. Results obtained in test experiments agreed within 0·1 per cent. with those found by independent potentiometric titration. The acidity of the solution should be less than 0·2 *N* in nitric acid, or 0·1 *N* in sulphuric acid. In presence of acid, the colour change of the indicator is from yellow with excess of halide to gray with excess of mercury, but is not reversible, and therefore, under these conditions, mercury cannot be titrated with halide. Up to 5 grms. of potassium nitrate in 25 ml. of solution to be titrated had no effect, but with more than 0·5 grm. of potassium sulphate in the same volume, high results were obtained. Calcium and barium had no effect, but considerable interference resulted from the presence of zinc and cadmium. Large amounts of ferric ions caused indistinct end-points, but this effect could be overcome by adding potassium fluoride until no further fading of the iron colour was seen, and in this way good results were obtained in the titration of a mixture of 25 ml. of 0·1 *N* chloride solution and 20 ml. of 1*M* ferric chloride solution. The mercurous nitrate standard solution was found to remain unchanged in titrating strength only if a few drops of metallic mercury had been added. The mechanism of the indicator action is attributed to an exchange reaction, such as

$$\underset{\text{surface}}{Hg_2^{++}(Cl^-)_2} + \underset{\text{solution}}{2(B.P.B.^-)} \longrightarrow \underset{\text{surface (lilac)}}{Hg_2^{++}(B.P.B.^-)_2} + \underset{\text{solution}}{2Cl^-}$$

(B.P.B. = bromphenol blue).

If the chloride ions are in excess in the solution, the surface layers of the precipitate will consist mainly of mercurous chloride, and only a few indicator ions have a chance to be adsorbed. At the equivalence point, and especially in presence of a slight excess of mercurous ions, the chlorine ion concentration in the solution is so small that the exchange reaction, resulting in the colour change of the precipitate, can take place to a considerable extent. The indicator action is not considered to be due to a simultaneous adsorption of mercurous and dye ions on the surface of the precipitate. S. G. C.

Reactions of Chlorates. J. Amiel. (*Compt. rend.*, 1934, **199**, 787–789.)—Previous work of the author (*Compt. rend.*, 1934, **198**, 1033) showed that spontaneous ignition occurred in mixtures of the chlorates of barium or lead with sulphur in the presence of moisture. It is contended that the formation of chlorine dioxide as an intermediate product is sufficient to explain this effect. In this connection, the explosive property of mixtures of sulphur and chlorine dioxide is subject to a "mass effect," and is enhanced in the presence of organic matter such as paper, sugar, etc. With damp chlorate white phosphorus reacts explosively, whilst red phosphorus inflames after a short period. Powdered selenium or arsenic reacts with incandescence, but tellurium, antimony, bismuth, wood charcoal, graphite, tin, and the ordinary metals do not give this effect. The sulphides of copper, antimony, arsenic and tin, prepared by precipitation, react explosively or with incandescence with chloric acid or a chlorate of the magnesium series of metals. The mineral sulphides react less violently. Various reactions occur with organic substances in the presence of chlorates and sulphur or selenium. Thus aliphatic alcohols yield aldehydes, benzyl alcohol yields benzaldehyde and, ultimately, benzoic acid, whilst toluene yields benzyl chloride. S. G. C.

Microchemical

Micro-Potentiometric Titration. I. Titration in Macro-drops. K. Schwarz. (*Mikrochem.*, 1933, 13, 6–17.)—Potentiometric titrations are carried out in a drop of liquid suspended on a ring-shaped electrode, the comparison electrode dipping into the drop. A simple tapless micro-burette (Schwarz, *Mikrochem.*, 1933, 13, 1; abstr., ANALYST, 1933, 58, 422) is used for the titration. The potential is measured statically, without compensation by direct reading, using a Lindemann electrometer (F. Müller and K. Geissler, *Z. Elektrochem.*, 1931, 37, 857). *Detail.*—The ring electrode is constructed of metal suitable for the titration in question, *e.g.* such as silver for argentometric titrations. It is made of wire, 0·3 mm. in diameter, and has an outer diameter of 4 mm. Stirring is effected by attaching the electrode through insulation to an ordinary radio loud-speaker system, when it is set in vibration by the 50-cycle A.C. current regulated by a suitable resistance, so that the voltage is about 30. Since in most of the titrations only the relative value of the potential is required, a comparison electrode giving a constant potential is used. This consists of a glass capillary, 0·8 mm. in diameter, into one end of which is sealed a small piece of platinum wire, and on the end of this about 2 mgrms. of silver are stuck. The free end of the capillary is drawn out to a finer capillary, about 4 cm. long, 0·3 mm. in outer, and 0·05 mm. in inner diameter. The capillary is filled with 0·001 *N* silver nitrate solution, with 0·1 *N* potassium nitrate in the fine capillary, for silver titrations. When the platinum ring-electrode is employed a comparison electrode of pure platinum, filled with 0·001 *N* sodium thiosulphate, is used. The platinum electrode is used as a hydrogen electrode for p_H determinations, especially in the alkaline range. Before the titration is carried out a drop of water (about 0·02 ml.) is placed in the ring electrode, and the tip of the comparison electrode is carefully placed in the drop. A measured amount of the solution to be titrated is added from one of the micro-burettes, and the titration is carried out by means of a second burette; the stirring is started immediately before the titration. Results are given for argentometric titrations with 0·001 *N* potassium bromide and silver nitrate solutions, whereby amounts of the order of 0·3γ of bromine are determined, with a maximum error of under 1 per cent.; with 0·0001 *N* solutions, amounts of the order of 0·03γ of bromine are determined with a maximum error of 4 per cent. With 0·01 *N* solutions of sodium chloride and silver nitrate, amounts of the order of 1·5γ of chlorine are determined, showing a maximum error of 0·5 per cent., and amounts of silver of the order of 5γ with a maximum error of 1 per cent. For the titration of sulphuric acid and sodium hydroxide, in which the platinum ring-electrode is used as an oxygen electrode, titrations were carried out on 0·001 to 0·005 ml. of 0·1 *N* sulphuric acid. At the same time the colour-change with 0·0001 ml. of alcoholic phenolphthalein solution was observed; the two series of results agreed well. Titrations were also carried out between lead nitrate (0·01 *N*) and potassium ferrocyanide (0·008 *N*) for the determination of about 5γ of lead, with an accuracy of about 0·5 per cent.; with ferric chloride (0·01 *N*) and potassium ferrocyanide (0·008 *N*) for the determination of about 1γ of ferric iron, with errors of less than 2 per cent.; for the determination of iodine by means of sodium thiosulphate with starch as indicator, and electrometrically with the platinum ring-electrode; and of arsenious acid with potassium bromide and potassium bromate in strongly acid solution, with the use of the platinum ring-electrode. J. W. M.

Micro Copper-Pyridine Reaction for Saccharin. C. Van Zijp. (*Pharm. Weekblad*, 1934, **71**, 1146–1151). **J. J. L. Zwikker.** (*Id.*, 1151–1152.)—A reply to the criticisms of this method by Zwikker (cf. *id.*, 1933, **70**, 553), based on a study of the optical properties of the crystals formed in the reaction (*id.*, 1934, **71**, 850). Determinations of the refractive index in both directions of the crystal and of the angles of the crystals indicate that prisms and needles may occur together in the same preparation; the different types of crystals and their optical characters are shown diagrammatically. Zwikker suggests that hexagonal plates may be built up from a number of shorter prismatic crystals. J. G.

Physical Methods, Apparatus, etc.

Studies in the Composition of Coal. A Method of Determining the Decomposition Point of Bituminous Coal. H. W. Hibbott and R. V. Wheeler. (*J. Chem. Soc.*, 1934, 1084–1086.)—The decomposition point of bituminous coal, which is the temperature at which breakdown of the structure of ulmins begins, is of value in being characteristic of the "rank" of the coal. A rapid method of determination, which is based on the sudden change that occurs in the quantity of gases yielded by the coal when its decomposition point is reached, involves raising the temperature of 1-grm. charges of the finely divided coal at the rate of 0·5° C. per minute, and measuring periodically the volumes of gases withdrawn by a vacuum pump. From the graph obtained by plotting the yield of gases against the temperature, the decomposition point can be assessed. The value obtained is a relative one, since the temperatures found by this method for a range of coals were 10° to 15° C. higher than the absolute values obtained by a lengthy method involving very slow heating (Holroyd and Wheeler, *J. Chem. Soc.*, 1928, 3197), and the absolute values can therefore be estimated with sufficient accuracy by subtracting 12° from the temperature indicated by the rapid method. With the exception of one sample of coal, which was also abnormal in other respects, the decomposition point was found to rise with the carbon-content of the coal, rising from 312° C. (relative) at 77 per cent. of carbon to 374° C. (relative) at 89·8 per cent. of carbon. S. G. C.

Use of Dioxan as Solvent in the Determination of Molecular Weights by the Cryoscopic Method. A. E. Oxford. (*Biochem. J.*, 1934, **28**, 1325–1329.)—The use of dioxan as a solvent in the cryoscopic method of determining molecular weights is recommended, as it is chemically inert and has wide solvent powers. Most crystalline organic substances, including many natural products other than sugars and amino acids, are soluble in dioxan, which has a freezing-point of 11·67° C. and a molecular-depression constant of 47. S. G. S.

Reviews

INTRODUCTION TO PHYSIOLOGICAL CHEMISTRY. By MEYER BODANSKY, Ph.D. Pp. x + 622. Third Edition, re-written and re-set. New York: John Wiley & Sons, Inc. 1934. 25s.

The name of Professor Bodansky is well known in biochemical circles on both sides of the Atlantic. His *Physiological Chemistry* bids fair to become a standard work. A criterion of standard works is the regularity with which they go into new editions; Professor Bodansky's book has already run through two editions in eight years, a very creditable result for a new-comer. Unlike many books reaching this country from the United States, this volume gives extraordinarily good value for money. Quite apart from the number of pages, which is generous in the extreme, the information is well up to date, and also covers the latest knowledge of the chemistry of vitamins *C* and *D*. Even the old view, that tachisterol is formed by a side reaction from lumisterol, has been corrected to conform with Windaus's more recent concept of a single chain of transformations, though the old C_{27} formula for ergosterol has not been corrected.

Needless to say, the sections on carbohydrates use the modern method of representing sugar structure, while the chapter on intermediary metabolism of carbohydrates discusses in considerable detail the highly complex chemical changes that take place during the release of energy in muscle fibre.

It is some indication of the author's sense of proportion that the author-index contains 43 references to the work of Mendel, 13 to the work of Meyerhof and only 4 to his own. Large though the number of textbooks on physiological and biological chemistry, it is impossible to resist the conclusion that this is one of the most valuable of all, both absolutely, and relatively to its price.

A. L. BACHARACH

MANUAL OF BIOCHEMISTRY. By J. F. MCCLENDON. Pp. vii + 381. New York: John Wiley & Sons, Inc. 1934. 31s.

Professor McClendon's book contains on page 4 the statement that "Vitamin *C* is ascorbic acid, one of the fatty acids, and is listed under that group," and on page 5 the statement that "Vitamin *D* is considered to be an isomere (*sic.*) of ergosterol, and is listed with the terpenes." The reader, having turned for consolation from these statements to the imposing-looking tables, printed on tough bluish-grey paper, that divide the end of the book from the author-index, finds that, in a list presumably meant to give accurate information on the substances in which biochemists are interested, ascorbic acid (or vitamin *C*) is not mentioned at all, and the only reference to vitamin *D* is under Viosterol, an American trade name for irradiated ergosterol, and not for crystallised vitamin; furthermore, to this is attributed a molecular weight of 382·32! The figure is not even correct for ergosterol or calciferol, and is quite meaningless for the oil solution of the mixture of substances constituting Viosterol.

Professor McClendon's book contains sixty per cent. of the number of pages in Professor Bodansky's *Physiological Chemistry* and costs twenty-four per cent. more, presumably by way of compensation. In the author-index there are four references to Meyerhof, five to Mendel, and eleven to McClendon. It is not at all clear to the reviewer exactly what public the publishers had in mind when they placed this book on the English market.

A. L. BACHARACH

A COMPREHENSIVE TREATISE ON INORGANIC AND THEORETICAL CHEMISTRY. XIII. By J. W. MELLOR, D.Sc., F.R.S. Pp. viii + 948. London: Longmans, Green & Co. 1934. Price 3 guineas.

The whole of this volume is devoted to the metallurgy, the physics and part of the chemistry of the iron compounds. The historical side of the subject was treated in Vol. XII. The new volume is probably Dr. Mellor's masterpiece. It is a stupendous work, and one that is based on innumerable references to the original literature. So far as the reviewer is aware, it is the most exhaustive treatise on iron that has yet been published. It is, indeed, a monument to the compiler's thoroughness and energy—characteristics which permeate the preceding dozen volumes. In one respect this volume is different from its predecessors in that it begins with a list of the errata found in the second, eighth and twelfth volumes. This list barely covers one-quarter of a page!

In the present volume the mechanical, thermal, optical, electrical and magnetic properties of iron occupy 297 pages; the chemical properties, 106 pages; alloys and intermetallic compounds, 175 pages; corrosion—a particularly fine exposition—91 pages; and 268 pages deal with the chemistry of some iron compounds. The only compounds considered are the oxides, their hydrates (including their colloidal chemistry), ferrites, ferrates, and perferrites.

We must heartily thank and congratulate Dr. Mellor on bringing his mammoth undertaking yet another important stage nearer to completion.

H. T. S. BRITTON

DETERMINATION OF REDUCING SUGARS BY FEHLING'S SOLUTION WITH METHYLENE BLUE INDICATOR. By J. H. LANE, B.Sc., F.I.C., and L. EYNON, B.Sc., F.I.C. Pp. 8. London: Norman Rodger. 1934. Price 4s. ($1) post free.

This monograph, bound in a flexible cloth cover, will be widely welcomed by all engaged in the volumetric determination of the commoner sugars by means of Fehling's solution. Few chemists are better qualified than the authors to produce such a brochure, for their long experience in the sugar industry and their extensive and careful investigations extending over many years have resulted in an accuracy and a precision hitherto unobtainable by the volumetric Fehling's method. That the results obtained by the methods described are reliable is shown by the fact that they have been adopted as standard procedures by various official bodies in different parts of the world.

The text is essentially practical in character, lucidly written and free from extraneous matter, while emphasising the necessity for exact standardisation of the method if accurate results are to be obtained. Directions are given for the preparation of the indicator, Fehling's solution and pure invert sugar solution by which it is standardised. The use of *neutral* lead acetate solution for clarifying the solution under examination and the removal of the excess of lead and calcium by means of potassium oxalate, together with the procedure adopted in the incremental and standard titrations with Fehling's solution, are given with all necessary detail. In this connection it is of interest to notice that the use of *basic* lead acetate as a clarifying agent and the presence of calcium salts in the liquid titrated are the cause of more or less serious errors.

The numerous tables give the values for each millilitre of the solution used in the titration over a range of 15 to 50 ml. for both 10 ml. and 25 ml. of Fehling's solution, and include invert sugar without, and with, various proportions of sucrose, dextrose, laevulose, and anhydrous and hydrated maltose and lactose; the corresponding values given are the "sugar factor" and the mgrms. per 100 ml. of the sugar present. Various applications of the method in commercial analyses are given, including those of raw and refined cane sugars, cane and beet molasses, starch dextrins and sugars, and sweetened condensed milks, together with two short tables of corrections for added invert sugar when only small amounts are present, and burette-reading corrections when lactose is determined in the presence of sucrose.

The whole compilation shows a high degree of accuracy, and is liberally provided with references to original papers, etc. Few persons other than chemists will appreciate the enormous amount of work entailed in the preparation of such a summary, and it is unlikely that for many years to come greater precision will be achieved in the volumetric determination of sugars. T. J. WARD

ROADMAKING AND ADMINISTRATION. P. E. SPIELMANN and E. J. ELFORD. Pp. x + 441. Figs. 142. London: Edward Arnold & Co. 1934. Price 25s.

It has been rightly claimed by a member of the Road Research Board that the transfer, rather more than a year ago, of the control of the experimental work on roads, conducted until then by the Ministry of Transport, to the Department of Scientific and Industrial Research, has led to closer contact between the men with practical experience and the scientific investigator. The construction and maintenance of roads involve uncertain factors which can be assessed only by those with practical experience. The scientific worker will, however, play an increasing part, if casual, disjointed trials are to give way to a well-planned, broad scheme of experiments controlled not only by road observations, but also by a comprehensive record of the chemical and physical properties of the separate constituents and the finished road material.

There are very few books on the highway engineering shelf which give more than a description of the standard methods employed in practice. Until recently it was difficult to trace original papers of value on the subject which appear in a wide variety of technical and trade journals, particularly as so many of these contributions contain a mass of practical data and relatively little co-ordinated scientific fact. A whole-hearted welcome must therefore be given to a volume under the authorship of an eminent civil engineer and of a research chemist who has spent many years in the study of road materials. The task was one worthy of the great amount of work it must have entailed, and, if we are not entirely pleased with the result, it will only be to admit that a valuable piece of work has been done and that it only requires polishing in the future edition which will undoubtedly be called for.

The authors have attempted to cover in one volume the whole range of roadmaking activities—Road Planning, Construction and Maintenance employing tar, asphalt, concrete, brick and rubber courses, Public Relations, Administration and

Law; it closes with Part VI, headed Scientific. This comprehensive survey is to form the first volume of a roadmakers' library. It is felt that as the more specialised volumes are issued, it will be possible to remove from the present book a certain amount of matter which leads to a lack of balance. This will improve what is otherwise an excellent and concise account of the present state of affairs and a useful indicator of the trend of modern developments. The authors have thoroughly combed the British and foreign literature and have produced a most useful bibliography containing 463 references. In general, the book seldom gives the full information required, particularly in relation to the laboratory examination of materials, but it does indicate where such information is to be found; hence its particular value to the analytical chemist.

It is a little hard to understand why valuable space should be taken up in a work of this nature, by a description of the equipment and running of a works laboratory, when this information is so readily available elsewhere, particularly as it is urged under the heading of "Staff" (p. 338) that a qualified chemist "fully conversant with his subject," and therefore fully capable of planning his own laboratory, should be engaged.

The binding, printing and general style are excellent, and very few typographical errors have been noted.

In summary, the reviewer welcomes the book, and, though not agreeing with the authors on many details, feels that the volume will be very frequently consulted as a valuable reference work.

F. M. POTTER

CONDUCTOMETRIC ANALYSIS. By HUBERT T. S. BRITTON. Pp. x+178. London: Chapman & Hall. 1934. Price 12s. 6d.

Although it seems unlikely that analysts will ever abandon for general work the time-honoured definite chemical methods of analysis, which yield unambiguous results because based on well-known reactions, they must always welcome new ways of carrying out old reactions, and more especially where they offer opportunities of studying the course of reactions where the time-factor is important. For this reason Dr. Britton's book may be found valuable by many whose direct interest in physical chemistry is small. He shows in it how many determinations may be carried out by conductometric methods, but it is unlikely that any large proportion of the methods described will be used in general analytical laboratories. All, however, are worthy of consideration where it is desired to make a large number of determinations of one kind under fairly closely defined conditions.

The apparatus described is not elaborate. A source of alternating current of reasonably high frequency, a simple Wheatstone bridge, which anyone can make with a few years of wire of high resistance a scale of length, and either a telephone receiver, or for the deaf a rectifier and a fairly sensitive galvanometer, with two small platinum electrodes kept during an experiment at a fixed distance apart, are all that is needed. By this simple combination of apparatus the darkest liquids may be titrated for acid or alkali, or the course of a slow reaction, such as the softening of water by Clark's process, can be studied, or the relative solid content of dilute solutions of similar groups of salts, such as drinking waters from the same source or condensates from steam-raising plant which may be contaminated with in-leaking cooling water, can be determined with sufficient accuracy and great rapidity. In fact, whenever a reaction between the substances dissolved in a liquid and those in another liquid, which is added to it, produces such changes in the number or mobility of the ions in the first liquid as to cause its conductivity to reach a maximum or minimum at the completion of the reaction, the end-point can conveniently be determined by following the conductivity changes occurring. It is necessary that the temperature of the liquid examined should be approximately constant, and that the amount of liquid added should not seriously change the volume in which the reaction occurs. This implies the use of relatively strong standard solutions and micro- or semi-micro burettes. Conductivity determinations of wash-water are useful for determining the completion of the washing of precipitates.

Dr. Britton has described clearly, in this small book, the essential principles underlying conductometric analysis, and has given numerous illustrations of processes based on these principles. He also, in Chapter XIV, shows, from his own and other workers' researches, how the course of reactions can be studied by conductometric methods. A final chapter on industrial applications usefully indicates some of these.

The arrows in Fig. 2 are so drawn that air could not be passed in the direction indicated without some disturbance of the reagents used for purifying it. The sign 15–16, page 26, is not usually considered equivalent to 15/16, which is intended, and a sentence on p. 28 suggests the immersion of a treatment rather than of the thing treated. The back-titrant, p. 140, is surely not 0·2 *N* NaOH but 0·2 *N* HCl, as shown in Fig. 41, and stated towards the foot of p. 141. These small slips in this useful and elegantly produced, if rather expensive, book will, it is to be hoped, soon be rectified in a second edition.

J. H. COSTE

AN INTRODUCTION TO PLANT BIOCHEMISTRY. By CATHERINE CASSELS STEELE, M.A., B.Sc., Ph.D. Pp. viii+356. London: G. Bell & Sons, Ltd. 1934. Price 15s. net.

Biochemists have in recent years turned more of their attention to plant chemistry, and this is mirrored in the number of books that have appeared on this subject lately. Dr. Steele has given us a very valuable summary of what is known up to date of plant biochemistry, and her book can be recommended to students of all classes. Special attention must be drawn to Part III, which deals with the sugars and similar substances. As is to be expected from a pupil of Sir James Irvine, this section stands well out.

The other parts of the book suffer, however, from the usual disadvantages of the *compiler*, and much is to be said against some of the statements that have been made about the tannins the anthocyanidins, and similar substances. However, it cannot be expected of an authority on the carbohydrates to be as well acquainted with other branches of the subject as Dr. Steele is with the chemistry of the sugars.

Of particular value is the Plant Index (pages 332–340) which is well arranged, since it gives not only the Latin name of the plant but also the common names, and indicates the chemical compounds present in the plants in question that are dealt with in the book. This should prove of much value to workers on this subject.

M. NIERENSTEIN

THE NATURAL ORGANIC TANNINS (HISTORY, CHEMISTRY, DISTRIBUTION). M. NIERENSTEIN, D.Sc., with Chapter on THE BOTANY OF THE TANNINS, by M. SKENE, D.Sc. Pp. 319. London: J. & A. Churchill, Ltd. 1934. Price 21s.

Dr. Nierenstein deals with the history of his subject with a thoroughness which is unusual in books on natural products. In this he has been helped by the fact that the ink obtained from galls and iron is mentioned in the works of the earliest writers. They were, however, not so interested in leather, and consequently Dr. Nierenstein's extensive historical researches have not yielded so many references to this more widespread application of vegetable tannins.

Our present restricted and uncertain knowledge of the chemistry of the organic tannins is described under three main headings: Catechins, Catechu-Tannins, and Condensed Tannins, Hydrolysable Tannins and Unclassified Tannins. Before the reader can choose between the rival views on the constitutions of catechin and of gallotannin—the chief subjects of the first two of these sections—he must fulfil the duties of counsel for the defence of the Freudenberg school and counsel for the prosecution of the Nierenstein school. For example, it is stated that some of the evidence put forward by Freudenberg in support of his constitutional formula of catechin is possibly invalid, because the constitution of cyanidin chloride is still an open question, although the synthesis of this compound by Pratt and Robinson and its preparation by Willstätter and Mallison by the reduction of quercetin (the constitution of which Dr. Nierenstein regards as settled) is not discussed. Similarly, although the presence of sugars in most of the other hydrolysable tannins is accepted, Dr. Nierenstein remains unconvinced that glucose is an essential constituent of gallotannin. He considers leucodigallic acid to be the chief constituent of this tannin. This acid contains a carboxylic ester grouping, the ketonic group of which has been reduced to a secondary alcoholic grouping. Compounds containing such semi-reduced carboxylic ester groupings must be rareties, and in order to carry conviction to the reader, other examples should be quoted from the literature, or, if necessary, be produced in Dr. Nierenstein's laboratory.

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In the concluding chapter Dr. Macgregor Skene gives an account of the distribution of tannins in the plant world and in individual plants, and discusses their probable condition in plant cells, and their possible function as reserve food materials, as active agents in metabolism and as end-products of metabolism.

A similar chapter on the physico-chemical properties of the tannins would have linked the chemical chapters to this botanical chapter. The condensed tannins, for example, are more feebly acidic, tend to have larger molecules, are more photochemically active, and are less hydrated than the hydrolysable tannins. Both types of tannins form aggregates with complex carbohydrates, and the affinity of such aggregates for water and proteins differs from that of their components. From whatever aspect the organic tannins are studied, these properties are important, and some account of them in future editions would complete a book that will be consulted by all interested in these natural products.

H. PHILLIPS

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